REPORT OF PETROLEUM AND NATURAL-GAS BRANCH
FISCAL YEAR 1949

BY R. A. CATTELL AND OTHERS

Bureau of Mines
Information Circular 7551

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UNITED STATES DEPARTMENT OF THE INTERIOR
Oscar L. Chapman, Secretary
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James Boyd, Director

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by

R. A. Cattell and others[1]

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SUMMARY AND INTRODUCTION

Progress of Bureau of Mines research related to oil and gas during the past fiscal year has been marked by the publication of more than 40 reports on the various phases of the work. These include papers dealing with the production of oil and gas, transportation of gas, chemistry and refining of petroleum, thermodynamic properties of hydrocarbons, and the processing and utilization of helium.

As an additional service to Pennsylvania oil operators, a new suboffice was opened in Bradford, Pa., during the year. With this addition, the work of the Petroleum and Natural Gas Branch of the Bureau of Mines is now conducted in two large stations, the Petroleum Experiment Station, Bartlesville, Okla., and the Petroleum and Oil Shale Experiment Station, Laramie, Wyo., and three field offices and laboratories at San Francisco, Calif., Dallas, Tex., and

Franklin, Pa., and two suboffices, Wichita Falls, Tex., and the newly opened suboffice at Bradford, Pa. In addition, this Branch operates large-scale helium-production plants in Texas, Kansas, and New Mexico, and maintains extensive helium-bearing gas reserves in Texas and New Mexico. All helium operations are supervised from headquarters at Amarillo, Tex. A small headquarters staff is in Washington, D. C.

A backward glance at the road traveled during the past several years by the Petroleum and Natural Gas Branch of the Bureau of Mines brings out a general background for the events of the fiscal year 1949. Throughout the fiscal year 1945, the activities of the Branch were still mainly concerned with such war activities as making special field studies for the Petroleum Administration for War, finding ways of increasing rates of production, and supplying data pertaining to the manufacture of aviation and jet-propulsion fuels. A period of adjustment came in 1946, characterized by a turning from war to peace procedures and efforts to give wide distribution to technical facts obtained in wartime research; also, there came a realization that the demands of war had broadened the horizons of research. This was emphasized in 1947, when a peacetime program was restored, based upon the long view of the Bureau's place as a research agency in oil and gas. Close attention was given to technical detail in 1948, and emphasis was placed on maintaining a balance between the industrial need for technical knowledge and Governmental-research possibilities in the fields of (1) withdrawal of petroleum from natural deposits, (2) utilization of petroleum and its products, and (3) commercial utilization of helium.

Studies of petroleum production and utilization and helium production and utilization are the normal functions of the Branch. These functions (sometimes expressed in different words) have been the mainstay of this organization since initiation of the work. The details of approach vary with changing conditions, but, fundamentally, the functions have been the same in both peace and war.

The work of the past fiscal year has emphasized the advantages that accrue when Government and industry join in a wise use of technical and scientific knowledge gained through research. Outstanding evidence of the beneficial results of cooperative effort by the Bureau of Mines and various organizations is found in the following typical examples, the details of which are discussed in the body of this report.

Working in close cooperation with operators along the Gulf Coast, the Natural Gasoline Association of America, and the National Association of Corrosion Engineers, the Bureau found, through field testing, that corrosion protection by means of chromates in high-pressure gas-condensate wells costs less than $1 per million cubic feet of gas produced. Laboratory experiments to measure the corrosion effects of carbonic and propionic acids on various steels and alloy steels gave data that will serve as guides in the selection of new materials for the construction of well equipment to be tested by industry under actual service conditions.

The cooperative work of the Branch with the Natural Gas Department of the American Gas Association has a long and full history, which need not be reviewed here. Studies from which mutual benefit has been derived and which are reported in following sections deal with the characteristics of gas-condensate fluids, measurements of productivity of high-pressure oil and gas wells (requiring the accurate measurement of subsurface pressures in wells), natural-gas hydrates, the flow of natural gas in pipe lines, and the removal of nitrogen from natural gas.

Cooperation in the field of secondary recovery research likewise has been widespread. In addition to financial support from such agencies as the State of Oklahoma, Kansas State Board of Health, Arkansas Oil & Gas Association, Pennsylvania Grade Crude Oil Association, and the North Texas Oil & Gas Association, the unstinted technical advice of the Secondary Recovery Advisory Committee of the Interstate Oil Compact Commission has been highly beneficial in maintaining an objective program, and this has been supplemented by the aid and assistance of many agencies, companies, and individuals.

An outstanding feature of the year was the starting of a program of fundamental research on the nature of the surface forces in petroleum reservoirs. This need for better understanding and control of the interfacial forces acting at the rock-water, rock-oil, water-oil, water-gas, and oil-gas interfaces is readily apparent when it is realized that these are the forces that usually restrict the recovery of the oil from the reservoir rocks in which it is found.

Another major activity was started, which, like the one just mentioned, pertains not only to secondary-recovery techniques but also to primary extraction. This problem deals with the effects of explosives upon porous rocks, more commonly called "oil-well shooting." Heretofore, this subject has been treated by industry mainly from a statistical and empirical viewpoint. The problem is now being approached by the Bureau from the viewpoint of the rock physicist as well as that of the petroleum engineer.

In the field of chemistry and refining, a balanced program supported by industry is exemplified in the work on the combustion of fuels. Particularly an understanding of the relationships of the composition of Diesel fuels and their combustion characteristics moved forward another step. This work has a number of industrial connections, covered both by formal and informal types of agreements. Nongovernmental agencies particularly concerned are the Western Petroleum Refiners Association, the Coordinating Research Council, Inc., and manufacturers of engines. With this support, several Diesel fuels were analyzed in considerable detail; in particular, a fairly complete picture of the composition of a Diesel fuel prepared from West Edmond crude oil was obtained. Correlated with this, the development of a constant-volume combustion-bomb has gone forward to such an extent that it now gives promise of yielding important information regarding the ignition characteristics of the hydrocarbons and their mixtures that go to make up Diesel fuels. The Coordinating Research Council, Inc., and the Department of the Navy contributed financial support to this work.

Another activity is the sulfur program of the Bureau, which is tied in closely under formal cooperative agreement, including financial support, with API Research Project 48-A on "The Production, Isolation, and Purification of Sulfur Compounds and Measurement of Their Properties." The research is being conducted as three independent but related projects, which are:

1. Synthesis, Purification, and Determination of Properties of Sulfur Compounds.

2. Determination of Thermodynamic Data of Sulfur Compounds.

3. Separation, Isolation, and Identification of Sulfur Compounds in Crude Oils.

Although high-sulfur crude oils have always been troublesome, the recent interest which the petroleum industry has shown in the better utilization of these crude oils points directly to the continuing need for this work.

The advance of petroleum technology must be based upon a sound fundamental knowledge of the chemical, physical, and thermodynamic properties of the materials involved in the manufacturing processes. Hence, petroleum chemists and chemical engineers are constantly demanding more and better data to aid them in devising better and more efficient processes. To aid in the accumulation of these data, the Bureau has continued its investigations to determine accurate values of the thermodynamic properties of hydrocarbons and related substances. An important part of the program is to determine systematically the thermodynamic properties of organic sulfur compounds.

Continued research on helium utilization indicated that helium purity would have to be increased, particularly in those cases where it is used in welding aluminum and certain other metals and alloys. Accordingly, for the second consecutive year, helium purity was increased substantially. In 1948 it was raised from 98.2 percent to 99.8 percent. In the past fiscal year it was increased further to 99.95 percent for all uses requiring such purity. Natural-gas analyses were continued in the survey to determine the Nation's total helium resources.

In each of the major types of work in which the Branch is now engaged, representatives of cooperating agencies exercise definite helpful stimulus to the technical advancement of the problems, as shown in the more detailed descriptions of the individual problems that follow.

ACKNOWLEDGMENTS

This information circular is based upon reports prepared by the scientific staffs of the six field headquarters of the Branch, which are under the immediate direction of the following supervising engineers:

H. C. Fowler, Petroleum Experiment Station, Bartlesville, Okla.
H. P. Rue, Petroleum and Oil Shale Experiment Station, Laramie, Wyo.
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C. B. Carpenter, Petroleum Field Office, Dallas, Tex.
S. S. Taylor, Petroleum Field Office, Franklin, Pa.

The oil and gas industry has given the Bureau of Mines splendid cooperation in connection with the research on petroleum, natural gas, and helium. Grateful acknowledgment is made of this assistance. Nineteen cooperative agreements were in effect during this fiscal year. These aided the research program greatly and accelerated progress. For this hearty cooperation and assistance by the State of Oklahoma, the Kansas State Board of Health, the Arkansas Oil & Gas Commission, the University of Wyoming, the College of Physicians & Surgeons of Columbia University, the Harvard Medical College, the Texas Technological College, the American Petroleum Institute, the Coordinating Research Council, Inc., the Natural Gas Department of the American Gas Association, the Natural Gasoline Association of America, the Pennsylvania Grade Crude Oil Association, and the North Texas Oil & Gas Association, the Bureau of Mines makes this acknowledgment and expression of appreciation.

Figure 1 shows the Bureau of Mines Petroleum and Oil Shale Experiment Station at Laramie, Wyo. The cornerstone was laid in 1945, and the building was completed and occupied in 1947. It adjoins the University of Wyoming campus and conforms architecturally with other buildings on the campus.

OIL AND GAS DEVELOPMENT AND PRODUCTION

Characteristics of Gas-Condensate Fluids

The objective of the research on the correlation of physical and chemical properties of gas-condensate fluids for the past year has been the preparation of a bulletin-type report that will include all of the data obtained during the war with the mobile laboratory in the field supplemented by laboratory data obtained to date with the equilibrium cell. The appendixes to this report will include an article, now almost complete, entitled "Critical Constants of Components of Gas-Condensate Fluids," a compilation of the best-known data from the literature on critical constants of hydrocarbons. It will be useful in correlating data obtained on natural hydrocarbon systems by means of the mobile laboratory. Also included will be an article entitled "Phase Equilibria Factors at Separator and Stock Tank Conditions." This will present averages of data relating to gas-liquid phase equilibria at atmospheric temperature and pressures up to 1,500 p.s.i.a. These data will serve three immediate purposes in the preparation of the bulletin: (1) Facilitate computation of fluid volumes at atmospheric pressure and temperature needed in compressibility studies, (2) serve as a step in one of the correlations of phase properties, and (3) provide a basis for defining a standard stock-tank condensate. The

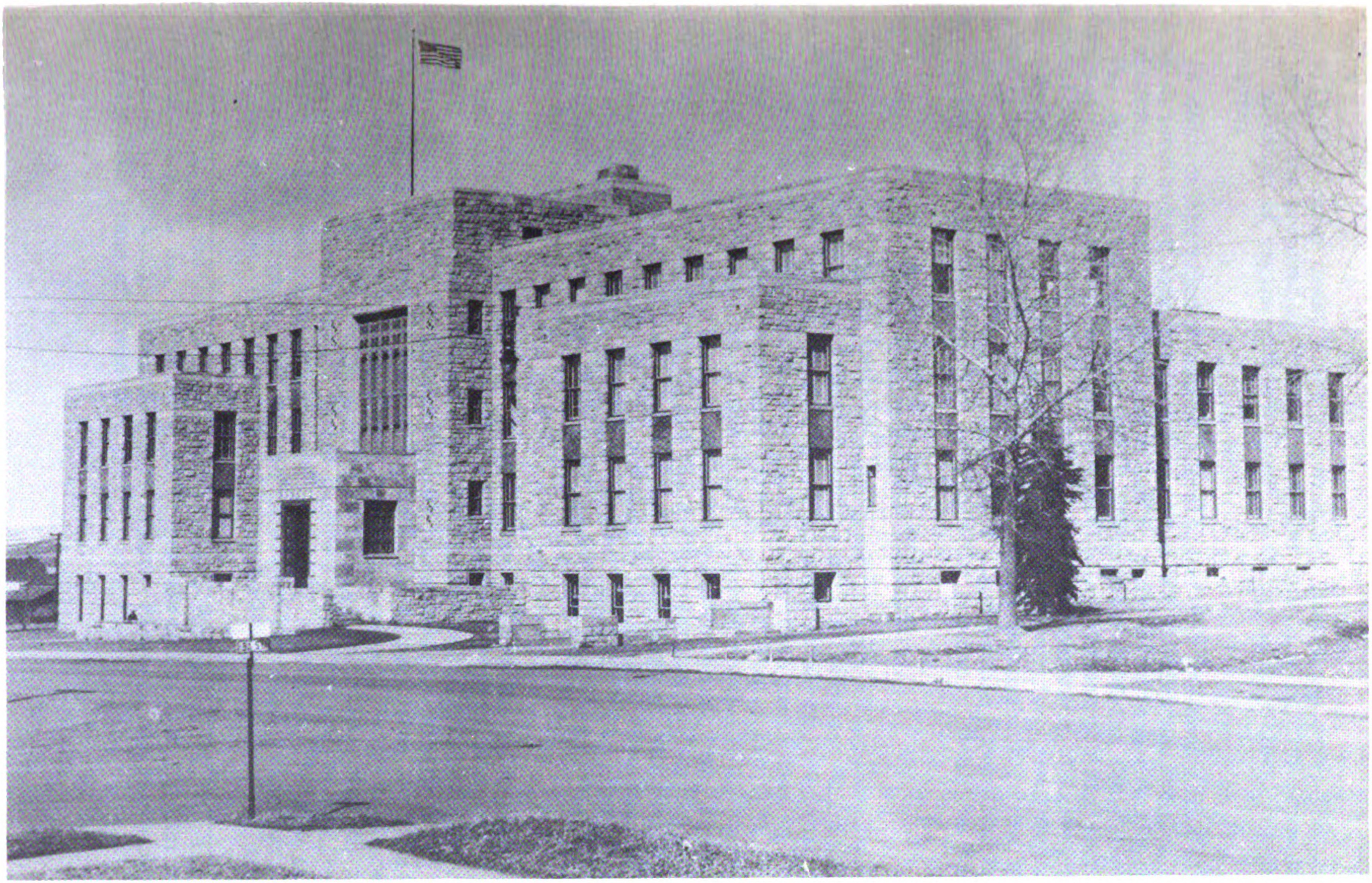

Figure I. - Petroleum and oil-shale experiment station of the Bureau of Mines at Laramie, Wyo. This building is adjacent to the University of Wyoming campus.

data will have other uses, also; for example, item 3 can serve the needs of industry in the preparation of contracts for settling royalty payments and aid in the solution of engineering problems relating to the selection and use of separators.

As data on the physical characteristics of the gas-condensate fluids could not be determined at temperatures lower than 80° F. with the mobile laboratory, the windowed cell was designed and built to operate at temperatures as low as -90° F., so that critical pressures and temperatures of the fluids could be measured. Basic data on the phase properties of hydrocarbon mixtures at low temperatures are of importance in the design and operation of low-temperature gas-storage projects, a type of storage gaining favor for gas-distribution systems that must meet high peak demands. Also, the probable phase state of a gas-condensate fluid in the reservoir is of considerable importance to operators in determining the procedure by which the reservoir should be produced.

Gas-Condensate-Well Corrosion

The results of the experimental study of the use of chromates and alkalies for controlling corrosion in gas-condensate wells[2] were assembled in manuscript form and are in the process of being published. On the basis of corrosion-control operations in two fields, corrosion protection by means of chromates is estimated to cost less than $1 per million cubic feet of gas produced. The determination of the limits through which the treatment of the wells with chromates and alkalies could be varied without loss of required corrosion-control benefits involved the greater part of the experimental effort in the field. The pH of the liquid water flowing through the tubing was found to be important in controlling the conversion of soluble chromates to insoluble reduced chromium compounds; reduction of the inhibitor to insoluble nonprotective compounds occurred when excessive concentrations of chromates were injected into the flow stream.

Laboratory experiments were completed in testing the resistance of 32 steels and alloy steels to corrosion by carbonic and propionic acids, which are constituents of corrosive gas-condensate fluids. Carbon steels are the least resistant of all the metals tested, and steels containing less than 5 percent alloying components were as susceptible to corrosion as the carbon steels. Croloy 9 showed promise as a material for well tubing, and cast steel containing 12.48 percent chromium, now in use for Christmas-tree fittings, corroded at unusually low rates. The 18-8 chromium-nickel steels and the alloys containing 85 percent or more copper and nickel, useful in the manufacture of Christmas-tree fittings, were found to have very low rates of corrosion. Detailed tests were made to determine the effects of contact between dissimilar metals and to determine the effect of heat treatment on the corrosion resistance of chromium and nickel steels. A report has been drafted presenting the results of the laboratory corrosion experiments and has been submitted to the Metallurgical Subcommittee of the National Association of Corrosion Engineers. Future publication is planned in conjunction with other Subcommittee technical reports.

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[2] Eilerts, C. K., Smith, R. V., Archer, F. G., Burman, L. M., Greene, Faye, and Hamontre, H. C., Field Tests of Sodium Chromates and Alkalies for Controlling Corrosion in Gas-Condensate Wells: First of six parts published in July 1949 issue of World Oil.

Petroleum-Engineering Studies

Carthage Field, Tex.

In a continuation of the engineering study of the Carthage gas-condensate field in Panola County, Tex., a rough draft of a report for publication has been completed. The productive area of the Carthage field to July 1, 1949, has been increased, since its discovery in 1936, to approximately 300,000 surface acres and has 346 producing wells, of which 199 are dual completions. The prorated production from the field is approximately 500,000 MCF of natural gas and 7,000 barrels of liquid hydrocarbons a day. The published report on the Carthage field will include estimates of the volume of hydrocarbons initially in place in the Hill sand and Upper Pettit zone, which contained over 98 percent of the reserves of the field.

New Hope Field, Tex.

A petroleum-engineering study[3] of the New Hope field that was completed and will be published as a report of investigations will be the first report by the Bureau of Mines on a field in which pressure maintenance was applied successfully to oil-bearing reservoirs by water injection. Pressure maintenance by injecting water into oil-bearing reservoirs before they are depleted is a fairly new technique that was applied first in April 1943 in an oolitic limestone reservoir by operators in the Midway field, Lafayette County, Ark. The Bureau of Mines report on the New Hope reservoirs treats in great detail all the characteristics of one oolitic limestone and two sandstone reservoir rocks and their undersaturated reservoir oils, and the behavior of the three reservoirs, two of which are believed to be closed.

Lake Creek Field, Tex.

A study of the Lake Creek field, Montgomery County, Tex., was completed, and the results were published. This report[4] is an engineering analysis of nine high-pressure reservoirs in the Lake Creek field discovered in 1941, which includes estimates of the initial volume of gas and the recoverable hydrocarbon liquid and oil. Condensate-bearing gas is produced from 22 multiple-completed wells that penetrate sandstone beds of the Wilcox group, Eocene age, between depths of 8,800 and 11,000 feet. The relatively low permeabilities of the reservoir rocks were controlling factors in the development and operation of the Lake Creek field. Although the initial daily production was low, the high recoverable hydrocarbon liquid content of the gas (5.9 gallons per 1,000 cubic feet) made development of the zones economically desirable.

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[3] Carpenter, Charles B., Anderson, Kenneth F., and Cook, Alton B., Petroleum-Engineering Study of the New Hope Oil Field, Franklin County, Tex.: Bureau of Mines Rept. of Investigations 4594, 1949, 88 pp.

[4] Hill, H. B., and Vogel, Felix A., Jr., Petroleum-Engineering Study of the Lake Creek Field, Montgomery County, Tex.,: Bureau of Mines Rept. of Investigations 4319, 1948, 65 pp.

Many new types of packers, plugs, and complicated equipment were invented and developed to make dual and triple completions of wells in the Lake Creek field safe, practical, and economical. Condensate-bearing gas is "cycled"; that is, it is passed through a plant where liquid products are extracted by reducing the pressure and temperature, and the dry residue gas is returned to the reservoir to maintain pressure and displace the remaining condensate-bearing gas. Study of the Lake Creek field was begun originally at the request of the Petroleum Administration for War and was issued as a restricted report in 1944. Through the cooperation of the operating companies, the manuscript was brought up to date and issued in this formal report of investigations.

Sheridan Field, Tex.

The Sheridan field was discovered in 1940, and 34 possible subdivisions of porous and productive Wilcox strata of Eocene age have been recognized between the depths of 7,997 and 11,497 feet. Oil or gas showings were reported in strata comprising 11 distinct zones, and by December 1945 oil was being produced from the upper zone and gas condensate from three underlying zones. The productive strata, consisting largely of impure sandstones, are thin and tight in all the reservoirs, and their permeability is extremely low. The structure of the field is an anticline that is faulted along one flank; the largest and deepest reservoir outlines a proved area of 8,800 acres.

The report[5] describes and analyzes the development and operation of this field in which the cost of drilling and completing some of the early wells was as much as $300,000, although later wells were completed for about $165,000. Unforeseen conditions, including "work-over" jobs, contributed to the high cost of completing wells in the deep-seated reservoirs under pressures up to 5,000 pounds per square inch.

A gas-cycling plant costing $3,500,000 was designed to process approximately 100 million cubic feet of gas a day and to return the residue gas to the formations at a plant pressure of about 4,000 pounds per square inch. The average recovery of hydrocarbon liquid is about 2.7 gallons per 1,000 cubic feet of gas processed, and the plant products include natural gasoline, distillate, normal butane, propane, and isobutane. Most of the leases in the field have been unitized, and operation of the plant and the wells is under the supervision of the Shell Oil Co., principal owner of the Sheridan field. This study was begun by Bureau engineers in 1944 at the request of the Petroleum Administration for War and was continued after World War II through the cooperation of the Shell Oil Co. and other interested companies operating in the field.

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[5] Hill, H. B., and Vogel, Felix A. Jr., Petroleum-Engineering Study of Sheridan Field, Colorado County, Tex.: Bureau of Mines Rept. of Investigations 4367, 1949, 94 pp.

Study of Reservoir-Oil Samples

North Lindsay Field, Okla.

Publication of the results of analyses of subsurface-oil samples from the North Lindsay field, Okla., completed the generalized study of these samples.[6] Data were obtained from static and flowing tests on the wells in the field, and the important physical properties of the reservoir oil were determined by laboratory tests. These data are of special interest, as the production from the North Lindsay field exemplifies an unusual type of reservoir oil being found in the southeastern part of the Anadarko Basin, where for the past 4 years there has been intensive exploratory drilling to relatively deep horizons. Subsurface samples and well test data are valuable in selecting well-spacing patterns, estimating reserves, and determining future reservoir performance.

Dove Creek Field, Colo.

What appeared to be an important reserve of natural gas and condensate was discovered at Dove Creek, Montezuma County, Colo., late in 1948. In order to know how to operate this field in the best manner for recovering the maximum amount of condensate, the reservoir fluids were sampled, analyzed, and a report prepared for guidance in operating the field. The results of these laboratory researches aid in estimating the amount of reserves available and in determining what losses of condensate will occur as the pressure changes during withdrawals from the field. Thus, knowledge is provided for the maximum recovery, consistent with the economics involved, of a resource of vital importance to our economy.

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[6] Cook, A. B., Spencer, G. B., Bobrowski, F. P., and Dewees, E. J., Bureau of Mines Analyses of Subsurface Oil Samples from North Lindsay Field, McClain County, Okla.: Pet. Eng., vol. 19, No. 13, September 1948, pp. 158-168.

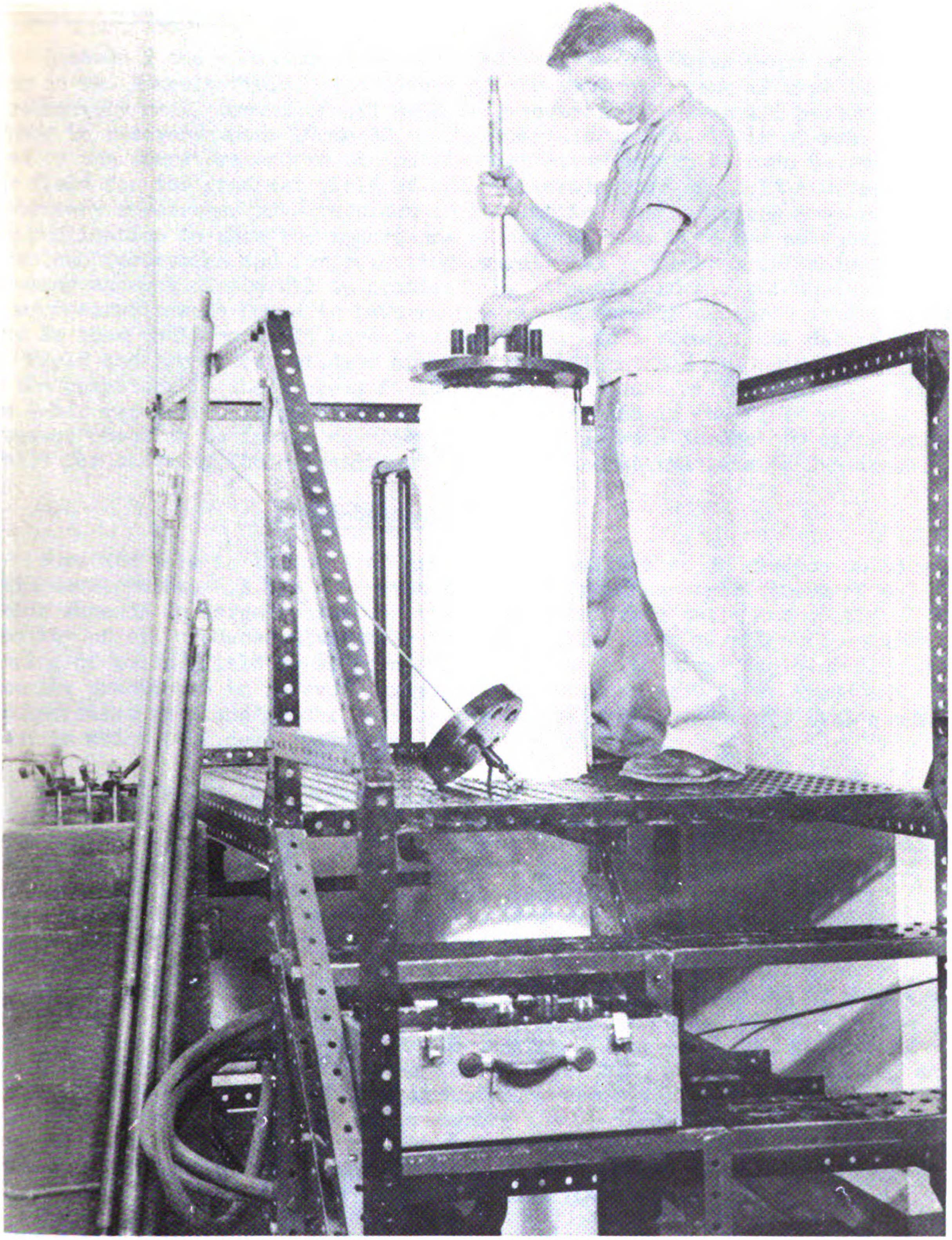

Figure 2. - Calibration well for checking field instruments, Laramie Station, August 17, 1948.

Rangely Field, Colo.

Between 2 and 3 billion barrels of oil are in the Weber sandstone reservoir in the Rangely field. The nature of the reservoir rock is such that only a relatively small amount of oil will be recovered. Because a 1 percent increase in recovery means 20 to 30 million barrels of oil, it is of real importance to the operators and to the public that every effort be made to operate the field for the greatest yield of oil. Several years of field studies and laboratory researches have resulted in information that is being prepared now for publication to show the importance of data of this kind for evaluating petroleum reservoirs and for selecting operational procedures suitable for recovering as much of the oil as practicable. The oil and gas throughout the Weber reservoir were found to have rather widely varying characteristics, much more so than would normally have been expected. As a result, the data from the field and laboratory studies are most significant and are being utilized by the operators in the Rangely field to obtain as much oil as possible from the Weber reservoir. Apparatus needed to obtain data in the field require frequent checking to insure accuracy. Figure 2 shows a laboratory calibration "well" for checking field instruments as installed at the Laramie Station.

Well-Spacing Studies

More and more is the cost of drilling oil wells a major expense in oil-field development. As the net revenue derived from the exploitation of oil fields depends in large measure on the cost of drilling wells and on the quantity of oil produced ultimately from the fields, the question of optimum spacing of wells (field development in accordance with sound engineering and economic practices) to recover maximum oil at minimum cost is an important consideration in planning the development of newly discovered oil fields and those in which full development initially was deferred.

Recognizing the importance of the well-spacing problem to the welfare of the public, the National security, and industrywide economy, Bureau of Mines engineers have continued the study started some time ago of the relationship between ultimate oil recovery and well spacing. The studies have proceeded along two different but interrelated lines; one engineer has devoted his entire effort on the problem to the collection and analysis of field data, whereas another engineer is making a theoretical analysis of the problem.

The results of the statistical study indicate that ultimate oil recovery, the spacing of wells, and the A.P.I. gravity of the produced oil are interrelated. The study reveals that the percentage of oil recovered ultimately from a reservoir is not much greater for 20-acre than for 40-acre spacing, and if the wells are deep and drilling costs high, apparently no worthwhile economic advantage is derived from reducing the spacing from 1 well to 40 acres to 1 well to 20 acres. The problem of optimum well spacing, however, assumes significance when it involves a decision whether to drill a property to a 40- (or 20-) acre spacing pattern or to a 10-acre per well or closer spacing, especially for low or less-than-average A.P.I. gravity oils. For such oils, 40 to 50 percent more oil will be recovered ultimately, on the average, if the fields are drilled to a 10-acre per well spacing pattern instead of 1 well to 40 acres; 60 to 85 percent more oil will be recovered ultimately, on the average, if the well density is 1 well to 5 acres instead of 1 well to 40 acres.

The Bureau's theoretical studies of well spacing have progressed to the point where the dearth of laboratory data on the flow of heterogeneous fluids through porous mediums and the complete lack of capillary-pressure data on three-phase flow systems necessitates developing a method for calculating the magnitudes of capillary-pressure gradients in such systems. Accordingly, in an attempt to gain information that may contribute to a quantitative explanation of the capillary forces that influence the motion of oil, water, and gas in an oil reservoir, a study is being made of the capillary behavior of three-phase fluids in static systems.

Drilling-Fluid Research

As the purpose of taking cores is to obtain fundamental information on the physical properties of the reservoir, it is necessary to obtain representative cores of the oil-bearing rocks. Methods have not been developed, however, that will permit cutting a core of an underground formation, which, when brought to the surface, is exactly representative of the formation from which it came. There is drilling fluid in the hole whenever cores are cut, and filtrate from this fluid enters the cores during the cutting operation and removes portions of the naturally contained fluids. In other words, the cores are contaminated by filtrate from the drilling fluid, and portions of their original fluids are flushed out.

To determine the degree of flushing of formation cores, Bureau of Mines engineers are continuing their studies of cores cut in wells in the presence of oil-base drilling fluids containing organic chloride tracers soluble in oil, insoluble in water, unaffected by bacteria, and stable at high temperatures. The results to date on cores from wells in the Mercy, Tex., Rangely, Colo., and South Coles Levee, Calif., fields and uncompleted tests on cores from a well in the Gulf Coast area and from shallow wells in the Appalachian region indicate that nearly all the cores contained filtrate from the drilling fluid that altered the oil content of the cores but did not affect their water content. Thus, by the method developed by the Bureau, a means is available for accurately determining the water content of oil-bearing rocks and, as the space in the cores not filled with water must be filled with oil (or oil and gas), the volume of petroleum in the reservoir can be calculated by subtracting the volume of water in the reservoir from the total pore volume of the reservoir.

One of the most important agents used by the petroleum industry to control the viscosity of drilling fluids is quebracho -- an extract from trees growing mainly in Argentina, S. A. During the last war, imports of quebracho into the United States were drastically curtailed, and the price rose to almost prohibitive heights. In this country, therefore, efforts are being directed to find substitutes for quebracho, and at the request of the Subcommittee for Quebracho Substitutes of the National Petroleum Council, Bureau engineers in the San Francisco laboratory tested 40 samples of materials that might be likely substitutes. Among the most promising substitutes for quebracho are industrial wastes from the lumber and wine industries, and those materials, which are inexpensive and seem to have desirable properties for controlling the viscosity of water-base drilling fluids, are being studied further as likely substitutes for the more expensive quebracho.

Cable-tool Coring with Improved Drilling Fluids

Most of the cores procured in the Appalachian Region are drilled with cable tools using fresh water as the drilling fluid. Ordinarily, laboratory analyses of these cores show lower oil content and higher water content than is considered representative of reservoir conditions, as is often proved subsequently by oil-production operations.

Owing to the vital importance of knowing the true oil and water contents of reservoirs in secondary recovery developments in the Appalachian Region, Bureau engineers have conducted field and laboratory investigations in efforts to apply oil-base mud (containing an oil-soluble tracer) to cable-tool coring in the hope that the resulting core-analysis data would more nearly depict reservoir conditions. A specially compounded oil-base mud was procured for the tests, and, in cooperation with oil companies, the seventh well was cored this year in Pennsylvania. Of the six wells cored last year when this investigation was started, one is in New York, three are in Pennsylvania, and two are in West Virginia. A different organic-chloride tracer (Aroclor 1254 - liquid), more soluble in the oil phase of the oil-base mud than used previously (Aroclor 1270 - solid), was employed in the last well cored. Before the results of the oil-base mud-coring studies are published, it is considered advisable to core one or two more wells. Premixed oil-base mud for these additional tests was procured.

To determine the impact pressure pulses occurring within a cable-tool core barrel during the coring of a sandstone, a rupture-type pressure gage was designed, constructed, and used once. In the well cored with oil-base mud, pressure pulses ranging from 200 to more than 1,500 p.s.i.g. were encountered during operation of the core barrel. The operator had previously removed the valves of this core barrel; hence, the pressures developed are considered lower than would have been found with inner and outer barrel valves in operation. With the development of such pressures during cable-tool coring, it is not surprising that the fluids native to the sand are contaminated or displaced with drilling fluid.

Productivity of High-Pressure Oil and Gas Wells

Research on the productivity of high-pressure oil and gas wells, begun in 1947 as an outgrowth of the earlier studies of gas-well gaging, has been directed toward the determination of the pressure loss due to friction in flowing gas wells. In the study of the theory of vertical flow in gas wells it was evident that the estimation of average temperatures and compressibilities of the flowing column of gas, required by the vertical-flow equations now in use by industry, resulted in the development of doubtful data on productivity. In an effort to eliminate assumptions as to average temperatures and compressibilities, an alternate method has been developed for computing friction factors for gas wells, which involves graphical integration of the mechanical-energy-balance equation over the actual path of the expansion of the fluid in the well. An article has been prepared for publication in the near future on this method of determining friction factors for measuring the productivity of gas wells.

As a positive solution of the flow phase of the gas-well productivity problem is possible only by experimentation, a field testing program has been outlined; to date, studies have been made on gas flow through the annular spaces between tubing and casing of two wells and on flow through the casing of two untubed wells. The test data were used to develop a tentative correlation between pipe size and friction factors for flow of gas in untubed gas wells. Also, the data permitted the calculation of friction factors for flow of gas in annular spaces containing 2-1/2-inch, non-upset tubing.

Calibration of Subsurface-Pressure Instruments

More accurate measurement of subsurface pressures is possible by following a procedure outlined from results of experiments on the calibration and use of a subsurface gage having a maximum reading of 1,200 pounds per square inch.[7] As a result of the study, improvements suggested in the calibration and use of the gage minimized or eliminated six avoidable errors and determined the extent of two inherent errors in the gage. In the range of 0 to 1,200 pounds per square inch, the accuracy of measurement was improved tenfold from an accuracy of approximately ± 5.0 to ± 0.5 pound per square inch. Bureau engineers believe that limitations of the mechanics of the gage tested prevent greater accuracy of measurement than ± 0.5 pound per square inch.

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[7] Smith, R. V., and Dewees, E. J., Sources of Error in Subsurface-Pressure Gage Calibration and Usage: Oil and Gas Jour., vol. 47, Dec. 9, 1948, pp. 85-98.

SECONDARY RECOVERY

With marked improvements in the economics of waterflooding for more profitable operation and in the availability of steel tubular goods for oil-field development, many of the larger oil companies now are entering into water-flooding activity along with the smaller operators. Consequently, in a number of large fields in the midcontinent that had been produced for many years by gas injection, such as the Burbank field in Osage County, Okla., and the Shoestring fields in Greenwood County, Kans., water-flooding operations on a large scale have been or will be instituted. This new and increased activity by less-experienced operators in the field of water flooding has increased the demand for published information on this and related subjects.

The present trend in the larger company operations is to unitize the leaseholds into large blocks for water flooding and to experiment with greater depths (to 4,000 feet) and with wider spacing of wells up to 1 well in 10, 20, and 40 acres.

Concrete developments aimed toward increasing ultimate oil recoveries from California fields by the injection of gas and water into reservoir sands are increasing in number and extent. Although most of the operations are of the pressure-maintenance type, in which extraneous energy in the form of natural gas under pressure is supplied to the reservoirs to maintain or partly maintain the reservoir pressure and thereby increase the recovery of oil by primary production methods, the possibilities of recovering additional oil from stripper fields by gas drive and waterflooding also are receiving consideration. Three waterflooding projects currently are operating in California in addition to 23 gas-injection operations in 19 fields. During the year, plans were consummated to study the currently operated gas and water-injection projects in California as a first step in a program of production research on secondary recovery of oil from stripper oil fields. This method of attacking the problem was selected after a preliminary study of gas-injection operations in California showed that there was no sharp line of demarcation between the ultimate aims of the different type projects, all of which had for their objective the recovery of more oil than was possible by primary-recovery methods without the injection of gas or water into the reservoir sands.

In the Appalachian Region, where less than 20 percent of the known oil-productive area has been subjected to any type of secondary recovery operation, it is highly important that operators know the probable gamble and reward they may expect by initiating gas-injection or waterflooding operations. Virtually all of the oil fields in the Appalachian Region have been depleted to the extent that most of the oil-driving gas energy has been dissipated, although tremendous quantities of oil yet remain in the sands. Thus, the main objective of the Bureau of Mines field engineering studies is to disseminate information by publication of all the records, including histories of development and operation on typical gas-injection and water-flooding projects that have been in operation long enough to prove the economic feasibility of these types of secondary recovery operations, so that operators of properties having comparable characteristics yet not exploited by secondary recovery operations, or only in part, can benefit by knowledge of the successful as well as the unsuccessful developments.

Field Studies

Petroleum engineering studies of stripper oil fields suitable for the application of secondary-recovery methods of production are an important part of the Bureau of Mines program related to secondary-recovery studies. Reports on these studies that discuss the geology, development, exploitation, and predictions of performance under secondary-recovery methods not only are invaluable to the operators in the fields studied but also serve as guides in many other fields. Figure 3 shows a Bureau of Mines truck, equipped with electrical logging equipment, used in oil fields of the Appalachian region.

Boggs Field, W. Va.

An engineering study of the Boggs field, Roane County, W. Va., completed in fiscal year 1948, was published.[8] This field was discovered in January 1911. The report gives an engineering appraisal of the 1,428-acre field, its development, and operation from date of discovery to date of probable abandonment and estimates of the probable total volume of oil to be recovered and the quantity of oil remaining in the sand. Surface maps of the properties and isopachous and contour maps of the sand are presented.

The engineering analysis shows that the cumulative oil production in 15 years of primary recovery operation amounted to only 8.54 percent of the original oil in place; that during both primary recovery and 19.5 years of secondary-recovery gas-drive operations, 13.28 percent of the original oil was produced; and that with 22 additional years of operation, using the same production techniques, the total volume of oil recovered would amount to only 15.25 percent of the crude oil originally in the reservoir.

This report significantly points out the need for unitization of all leases in all fields, particularly in the Appalachian Region, where secondary-recovery techniques of operation must be relied upon to exploit stripper oil properties to obtain the greatest ultimate recovery. Even with the Boggs field operated as it was during the primary recovery period, a greater ultimate recovery of oil could have been realized by secondary recovery gas-injection

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[8] Tignor, E. M., Jennings, Thomas, and Krause, Leon, Secondary Recovery of Oil by Gas Injection in the Boggs Field, Roane County, W. Va.: Bureau of Mines Rept. of Investigations 4430, 1949, 31 pp.

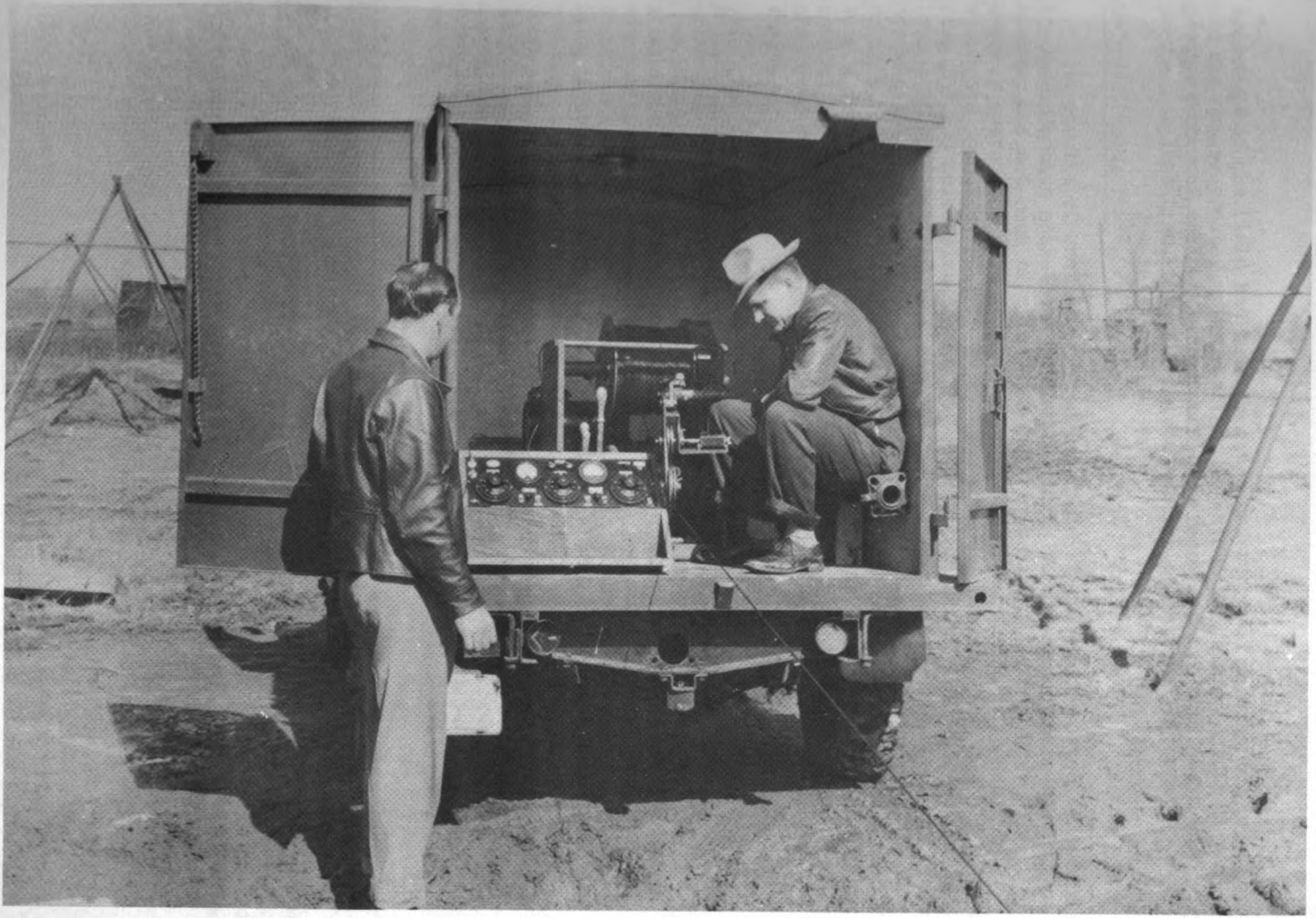

Figure 3. - Bureau of Mines field truck equipped with electrical logging equipment.

operations if the field had been operated under proved unitization principles and the same or greater volumes of gas injected into the reservoir through a greater number of wells. Furthermore, the recovered oil would have been produced in less time, thus saving part of the operational expense.

McDonald Field, Pa.

The results of another engineering field study were reported,[9] describing gas-injection operations in southwestern Pennsylvania, where secondary recovery has not been practiced extensively or intensively. Secondary-recovery operations were initiated in the McDonald field, Allegheny and Washington Counties, Pa., in 1932. The project comprises 29 leases having an area of 3,200 acres situated in the central portion of the 9,000-acre field. Because of the shortage of cheap natural gas and the reluctance of the operator to contaminate the low-pressure natural gas in the reservoir with air, only 650,716 cubic feet of natural gas was injected into the sand at pressures ranging from 65 to 100 p.s.i.g. through 12 injection wells during the 10-year interval covered by the report. Although the injected volume of gas was small and spread over a large area, the oil-production rate was stimulated on all 26 leases.

Atlanta Field, Ark.

In June 1949, the results[10] of a petroleum-engineering study of the Atlanta field, Columbia County, Ark., were released. Earlier, these data[11] were published in condensed form in a trade journal for more immediate availability and wider distribution. The Atlanta field is one in which fluid is being injected early in its life to effect a more efficient recovery of the contained oil rather than allow the reservoir pressure to drop to a point where much more energy is required to move the oil into the producing wells. The field, discovered in 1938, produces from the Smackover limestone at an approximate depth of 8,200 feet. The original reservoir pressure was estimated to exceed 3,800 p.s.i., and water injection was started in 1946, when the average reservoir pressure had dropped to about 2,900 p.s.i.

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[9] Tignor, E. M., and Nabors, Wm. M., Secondary Recovery of Oil in the McDonald Field in Southwestern Pennsylvania: Producers Monthly, vol. 8, No. 6, April 1949, pp. 20-26, 6 figs.

[10] Riggs, C. H., Petroleum-Engineering Study of Atlanta Oil Field, Columbia County, Ark.: Bureau of Mines Rept. of Investigations 4455, 1949, 55 pp.

[11] Riggs, C. H., Atlanta Field, Arkansas, Begins Second Decade of Production: Oil and Gas Jour., vol. 47, No. 41, Feb. 10, 1949, pp. 86-87, 89, 91-92, 94, 96.

Healdton Field, Okla.

One of the larger projects initiated during the year was a study of the Healdton field in Carter County, Okla. The study should serve to draw the attention of secondary-recovery operators to this neglected area and to provide many valuable data for future operations. The field includes 7,500 productive acres, on which 2,570 wells have been drilled. Although it was discovered in 1913 and developed during the next few years, 73 new wells have been drilled during the past 3 years. Principal production is from the Healdton sand. Cumulative production exceeds 200 million barrels of oil, but much of the oil sand remains highly saturated.

Weber Pool, Okla.

A petroleum engineering study of the Weber pool, Washington County, Okla., which is nearing completion, will be of interest to hundreds of operators producing oil from the Bartlesville sand in many fields in Oklahoma and Kansas. Discovered soon after the turn of the century at a depth of approximately 1,200 feet, it has been produced by gas-injection for many years, but it is estimated that the recoverable oil that remains in the reservoir exceeds the oil that has been recovered from the field to date. Figure 4, showing the distribution of the original reservoir fluids, indicates that an average barrel of pore space in the reservoir originally contained 31 percent connate water and 60 percent oil. It is estimated that $15\frac{1}{2}$ percent of the barrel represents stock tank oil already produced, 25 percent of the oil is not recoverable by present methods, and 20 percent is oil that may be recovered by efficient secondary-recovery methods. This will represent nearly 18 million barrels of recoverable oil, which at present prices is worth more than 45 million dollars.

History of Water Flooding in Oklahoma

Keeping pace with the ever-increasing demand by large and small oil operators alike for information on waterflooding, Bureau of Mines engineers continued to collect and assemble data for the revision of Report of Investigations 3728, "History of Water Flooding of Oil Sands in Oklahoma," published in 1942. The information compiled shows that as of the first of the calendar year (1949) there were in the State of Oklahoma 172 waterflooding projects controlled by 82 operators, as compared with 73 projects and 42 operators reported in 1942. These projects produced over $26\frac{1}{2}$ million barrels of oil to the end of 1948. The information also shows a marked increase in activity and interest by the larger oil companies and a trend toward deeper floods and wider well spacing by these companies.

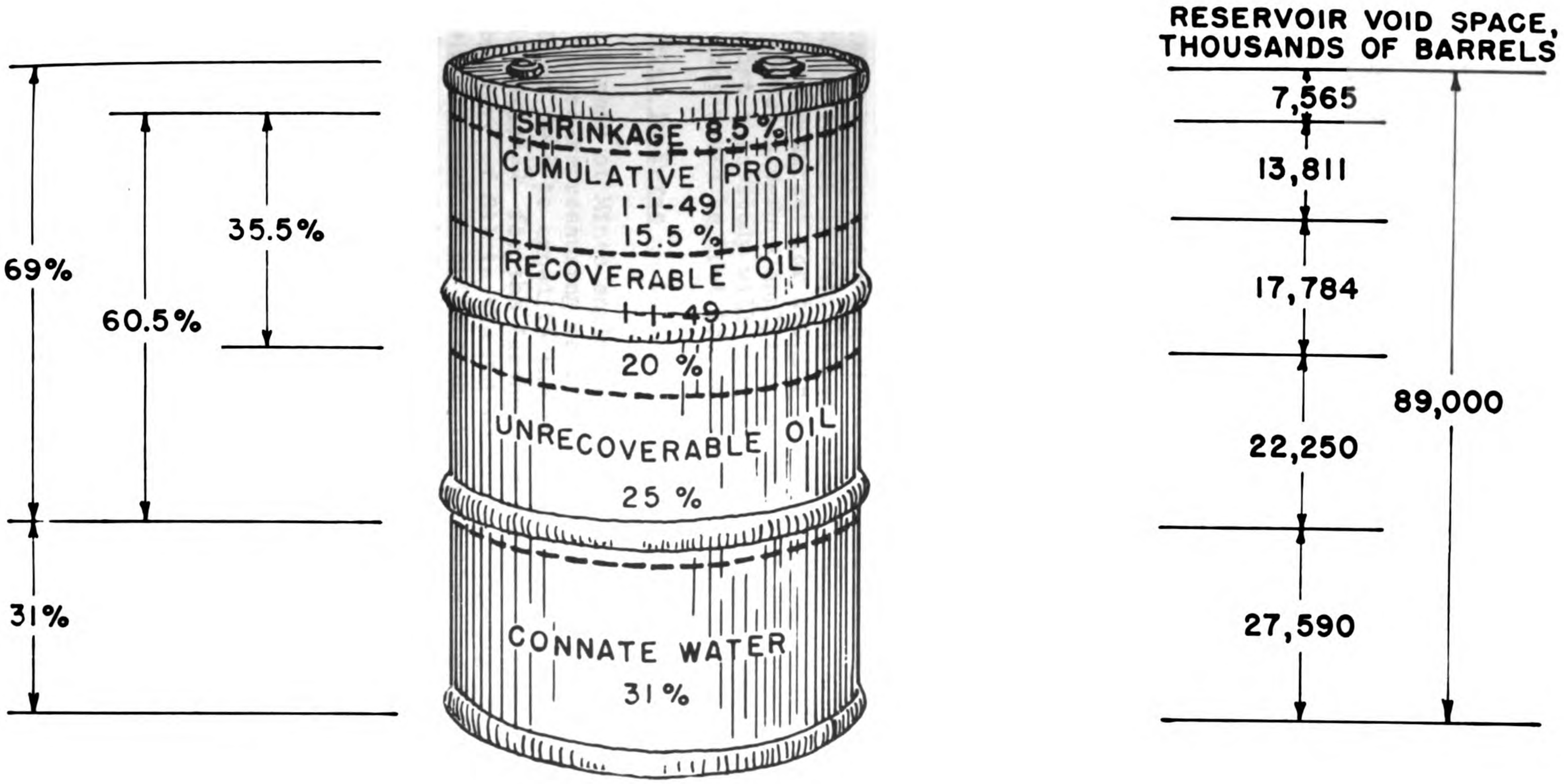

Figure 4. - Schematic drawing showing the fluid content of the average barrel of pore volume in the Weber Pool, Washington County, Okla.

West Red River Field, Okla.

Engineers of the Bureau of Mines and the Geological Survey completed a long-term study of the nearly depleted West Red River field, Tillman County, Okla.[12] A vast amount of detailed development and production data was collected between 1920 and 1925 while the land in the field was in receivership and supervised by the Bureau of Mines and subsequently while operations were supervised by the Geological Survey as part of the public domain. From the case history of this field the authors were able to draw some conclusions and to make certain recommendations that should be helpful to persons responsible for the operation of similar near-depleted fields in the North Texas region. The study also suggested the possibility of waterflooding the reservoir as a means of secondary recovery.

K.M.A. Field, Tex.

At the request of the North Texas Oil & Gas Commission Secondary Recovery Committee, Bureau of Mines engineers began a study of units 5 and 6 in the southwestern part of the KMA field in Wichita and Archer Counties, Tex. The area selected contains 12,000 acres controlled by 60 independent and major companies operating 135 leases. The KMA limestone has been subjected to pressure maintenance by gas injection since 1940, and the wells in the two units are producing less than 10 barrels per well per day. The high cost of operation and favorable market for tubular goods has resulted in the plugging and abandonment of wells before applying improved methods of secondary recovery. It is hoped that this study will suggest some method of economically recovering the oil that would be lost if the remaining wells are abandoned.

Gas-Repressuring in Texas

Because Bureau of Mines engineers desired to obtain as much information as possible on gas-repressuring in Texas, the services of one engineer were offered in March 1948 to expedite the preparation of the chapter "Gas Repressuring in Texas"[13] for the forthcoming revised edition of the API volume "Secondary Recovery of Oil in the United States" (1942). The Bureau engineer assisted the senior author of this chapter in collecting, assembling, and tabulating the requested information on 191 gas-repressuring projects representing 75 percent of the gas repressuring projects in Texas.

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[12] Hill, H. B., Johnston, Kenneth H., Coleman, T. L., and Seward, J. M., Petroleum-Engineering Study of the West Red River Field, Tillman County, Okla.: Bureau of Mines Rept. of Investigations 4450, 1949, 97 pp.

[13] Gouldy, Roland, and Dobyns, Rollie P., Gas Repressuring in Texas: Final manuscript approved for inclusion as a chapter in the forthcoming revised edition of the American Petroleum Institute volume "Secondary Recovery of Oil in the United States."

Special Field Problems

Location of Abandoned Wells

The detection of abandoned wells that were improperly plugged is one of the most perplexing problems when developing a new waterflooding project. Before adequate laws regarding plugging of wells were enacted, many abandoned wells were plugged ineffectively, and consequently these wells may leak oil and water to the surface or into shallow fresh aquifiers when the formation is subjected to water pressure. Bureau engineers now are investigating various means of finding these abandoned holes. An Army mine detector (see fig. 5) has been effective in locating, at depths to 12 or 18 inches, scrap iron that usually is scattered near old wells. The M-Scope pipe finder has been effective in following old lead lines that often are left buried in place, thereby marking the location of old wells. This device is effective to depths of 5 or 6 feet.

Conditioning Water for Subsurface Injection

The study of methods of treating and conditioning injection water to prevent plugging of the oil sands and to reduce corrosion of equipment was continued with the mobile laboratory unit. Treatments in use at four water plants in Kansas and six in Oklahoma were examined by determining hydrogen-ion concentration, carbonate stability, dissolved gases, suspended matter, and corrosive effect on special metal disks. In addition to providing valuable information to the operators on the effectiveness of their treatments, a manuscript[14] was prepared describing the treating methods used, the Bureau of Mines test procedures, and the results obtained on injection waters.

Input Rates and Pressures for Water-Flooding Oil Sands

The "injectivity index" and the "critical input pressure" of a water input well are important criteria of the intake capacity and the maximum pressure that may be applied without parting the formation and subsequent bypassing of water. A report[15] on a recently completed study explains that procedure used in making these determinations and gives the results obtained from input wells in nine sandstones that are being waterflooded extensively in mid-continent fields. The study shows that there is no "safe" rule-of-thumb

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14/ Watkins, J. Wade, Field Analyses and Corrosion Tests Applied to Waters used for Subsurface Injection: Manuscript approved for publication as a journal article.

15/ Grandone, Peter, and Holleyman, J. B., Injection Rates and Pressures for Water Flooding Mid-Continent Oil Sands: Bureau of Mines Rept. of Investigations 4600, 1949, 30 pp.

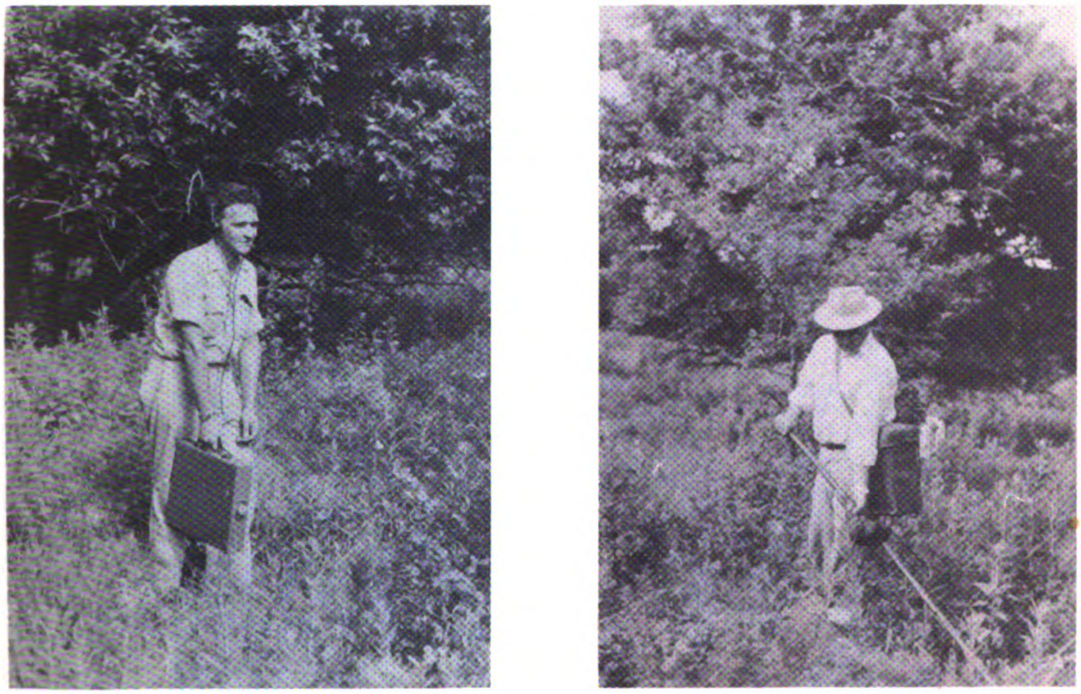

Figure 5. - Bureau of Mines engineers testing various types of equipment for detecting abandoned and improperly plugged wells on tract being developed for water flooding. At left, M-scope pipe finder is being used to follow abandoned lead line (18 inches underground) to reach location of abandoned well. At right, Army mine detector is being used to search for buried scrap iron usually found in vicinity of abandoned wells.

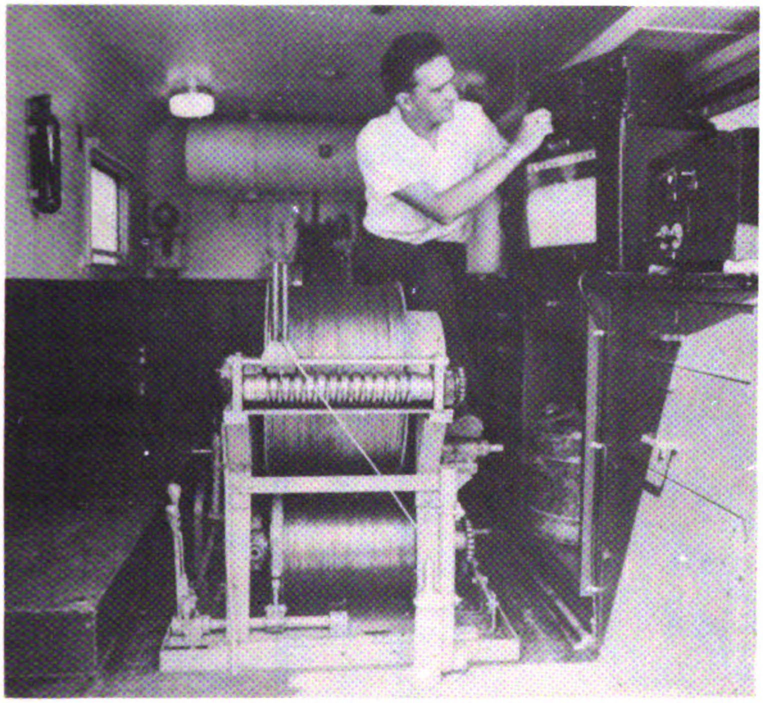

Figure 6. - Interior of Bureau of Mines mobile laboratory equipped for testing wells on secondary recovery projects. Measurements that may be made with this equipment include subsurface pressures and temperatures, input profiles, and electric logs.

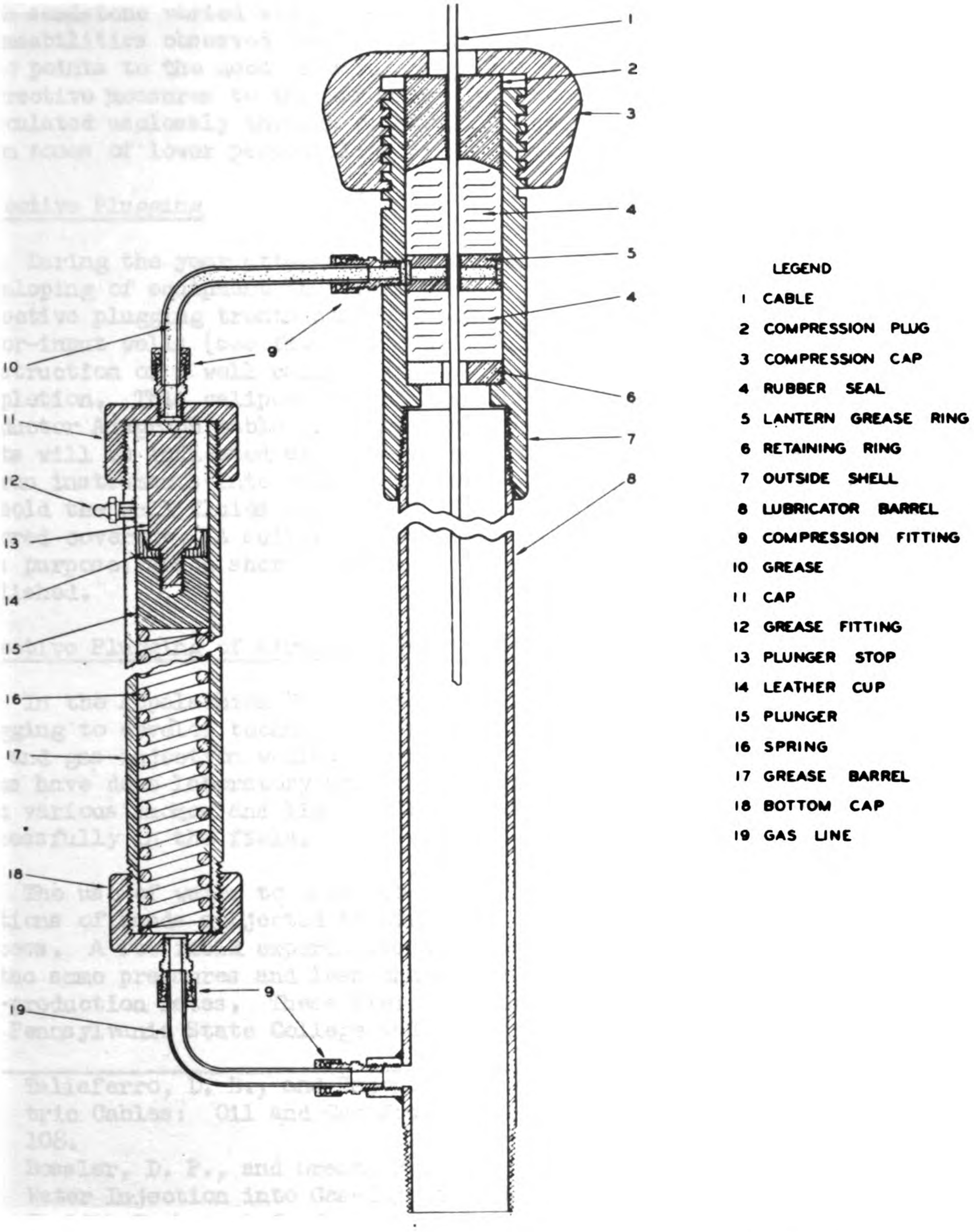

Figure 7. - Grease-packed stuffing box developed for armored electric cable.

injection pressure in any area and that the injectivity indexes of wells in each sandstone varied widely, as might be expected from the wide range in permeabilities observed from cores of each of these sandstones. The study also points to the need of developing better techniques for the application of corrective measures to the waterflooding process, because much water is being circulated uselessly through oil-depleted zones in an attempt to recover oil from zones of lower permeability in the same formation.

Selective Plugging

During the year attention has been directed toward the perfecting and developing of equipment that will permit the quantitative evaluation of selective plugging treatments by the measurement of the input profiles on water-input wells (see fig. 6). The liquid-level gage was improved, and the construction of a well caliper for use with the liquid-level gage is nearing completion. This caliper will be lowered into the well on the same single-conductor Amagraph cable provided for the liquid-level gage, and the measurements will be indicated at the surface. Frequently, when this cable is used to run instruments into wells that are under pressure, the pressure seal fails to hold the well fluids because of the irregular surface of the spirally wound armored covering. A suitable grease-filled stuffing box was developed for this purpose, and a short article[16] describing the device (see fig. 7) was published.

Selective Plugging of Air-Gas Injection Wells

In the Appalachian Region there is an urgent need for work on selective plugging to develop techniques for applying smokes and liquid suspensions in air and gas-injection wells. Pennsylvania State College and other organizations have done laboratory work on the plugging of small sandstone specimens with various smokes and liquids, but none of the products has been applied successfully in the field.

The use of water to decrease the effective permeability of fluid-depleted sections of sands subjected to air-drive has been tried in the field with some success. A few field experiments have resulted in lower gas-injection rates at the same pressures and less channelling of gas but without affecting the oil-production rates. These field experiments were made in cooperation with the Pennsylvania State College and resulted in a report.[17] The use of solid particles in suspension in water, or chemically treated water, is being investigated in the laboratory, with emphasis on considerations of how they can be applied successfully in selectively plugging gas-injection wells.

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[16] Taliaferro, D. B., and Hamontre, H. C., A Stuffing Box for Armored Electric Cables: Oil and Gas Jour., vol. 47, No. 32, Dec. 9, 1948, pp. 105, 108.

[17] Bossler, D. P., and Grant, Bruce F., Field Experiments with Intermittent Water Injection into Gas-Injection Wells on Secondary Recovery Projects: Twelfth Technical Conference on Petroleum Production of School of Mineral Industries, Pennsylvania State College, State College, Pa., October 14-16, 1948, 4 figs. In press.

Flowing of Oil Wells on Gas-Injection Projects

Progress was made on an investigation under study for several years to determine the fundamental characteristics of flowing through small-diameter, siphon-type flowstrings the oil produced from marginal wells on air-gas injection projects. Following some experimentation in the field, the technique proved feasible in wells 300 to 1,100 feet in depth. Such flowing has not been tried in deeper wells. After several years of development through laboratory and applied field research, the flowing of marginal wells in the vicinity of Oil City, Pa., is considered an improved oil-production technique and is practiced in several places where reservoir conditions permit.

Because flowing permits operating economies not possible with pumping wells, the availability of this technique may be of economic importance to operators of gas-injection projects in the Middle District of Pennsylvania and other parts of the Appalachian Region.

During this investigation the Bureau has provided instrumentation to acquire physical data required for an engineering appraisal of the feasibility and economic significance of this new oil-production practice. Enough data have now been developed to justify at least three engineering reports on this phase of the Bureau's investigations at Franklin, and a comprehensive report is being assembled.

Shooting Oil and Gas Wells with Explosives

A study of oil- and gas-well shooting was initiated this year. A threefold approach to the problem was started to determine how and why an explosive fractures oil- and gas-bearing rocks and thereby increases the productivity of shot wells: (1) A fundamental study to determine experimentally the mechanism of rock fracturing with the physical properties of the rock; (2) a survey to determine the physical properties of the oil-bearing rocks obtained from fields throughout the United States where well shooting is practiced, so that any correlations developed by the fundamental study may be applied directly to the shooting of oil and gas wells; and (3) an analytical study of present oil- and gas-well shooting practices in every producing area and the results as measured in terms of production rates before and after shooting.

To improve on the empirical methods now used in designing shots for oil and gas wells, it is evident that it will be necessary to explore the fundamental relationships governing the fracturing of rock under the conditions of well shooting. The Bureau, in its research program on mining, has been working during the last few years to determine the behavior of rock when subjected to dynamic or shock loading and has developed techniques of measuring the strain produced in rock by the shock wave resulting from an explosive detonated within the rock. These instrumentation techniques and knowledge of rock behavior have permitted an experimental approach to the problems of oil-well shooting that promises a direct correlation between the effects of different explosives (or between varying the methods of loading, tamping, and detonating any one explosive) and at least some of the physical properties of the rock as determined by laboratory measurements on core samples.

An experimental program was developed involving the shooting of small-diameter holes drilled to shallow depths in a sandstone sufficiently thick and with suitable lithologic properties. Gages were mounted around each experimental shot hole to determine the strain produced in the rock by the shot. These gages provide a means of judging the extent of fracturing to be expected, whereas injectivity tests made on the holes before and after shooting show the increase in conductivity resulting from the shot.

To test the validity of this approach, a series of tests was completed on a site where a 50-foot section of the Homewood sandstone (Pottsville group of lower Pennsylvanian age) occurs under a few feet of overburden. Four types of tests were run, as follows:

Designation	Type of test	Number of shot patterns
Series I	Linear array shots	One
Series II	Crater shots	Five
Series III	Instrumentation shots	Three
Series IV	Small scale well shots	Three

From the data obtained from these preliminary tests it will be possible to work out a future program of experimental shooting that can be expected to provide valid relationships affecting the design of shots for oil and gas wells to insure maximum increase in conductivity of the well (maximum fracturing), provided the physical properties of the oil- and gas-bearing rocks are sufficiently well known.

Laboratory Studies

Core and Water Laboratories

During the year the core and water laboratory made routine mineral analyses on 181 oil-field brines and made determinations for barium on 103 of these samples. Connate-water determinations were made on 190 samples of oil-well cores by the restored-state method, 67 samples were tested for permeability, and 55 for porosity. In addition to providing factual data on cores and oil-field brines required for research studies on secondary-recovery methods, a manuscript[18] was prepared describing the test procedure used for the determination of porosity. The method consists in determining the volume of the solids in the test sample by use of the gas laws and the bulk volume by mercury displacement.

Several results of real significance to the petroleum industry in the Rocky Mountain States will ensue from the establishment of studies and researches in the field of secondary recovery of oil. A knowledge of the physical characteristics of the formations that have produced oil in the many fields in the area will permit judging possible recovery operations in one field through comparison with operations elsewhere. To implement such studies, a laboratory was set up fully equipped to determine oil-bearing formation characteristics of porosity, air and liquid permeability, saturation, capillary pressure, and response to flooding agents. Studies of the almost depleted oil-bearing Frontier formation sands in the Grass Creek field, Wyoming, were initiated.

Oil-formation specimens procured in the Appalachian Region from wells drilled on secondary recovery projects and others obtained in connection with special scientific investigations of reservoir characteristics being studied by Bureau engineers were analyzed. Cores were tested, after preparation with special tools, for porosity, permeability, oil and water saturations, and the chloride content of the contained water. During the year one oil-well core was analyzed in connection with the oil-base mud cable-tool coring studies. Figure 8 depicts apparatus for determining the permeability of specimens prepared from core samples of oil-producing formations as used at the Franklin, Pa., field office.

Correlation of Residual Oil Saturation, after Laboratory Air-Drive Tests, with Pore Patterns of Sandstones

Laboratory experiments on air-drive expulsion of oil and water from "fresh" and laboratory-saturated rotary cores were conducted. The work was done with so-called flood pots, which were operated in a manner to simulate air-drive secondary-recovery operations in the field. One objective is to learn whether there is a relationship between the volume of oil retained in the sand core following the flood pot test and the shape, size, and distribution of the sand pores, taking into consideration the viscosity and temperature of the fluids used and the rock characteristics determined by routine core analysis on the same pieces of core used in microscopy tests. Each of 34

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[18] Rall, Cleo Griffith, and Taliaferro, D. B., A Bureau of Mines Method for Determining Porosity: A List of Porosities of Oil Sands: Bureau of Mines Rept. of Investigations 4548, 1949, 28 pp.

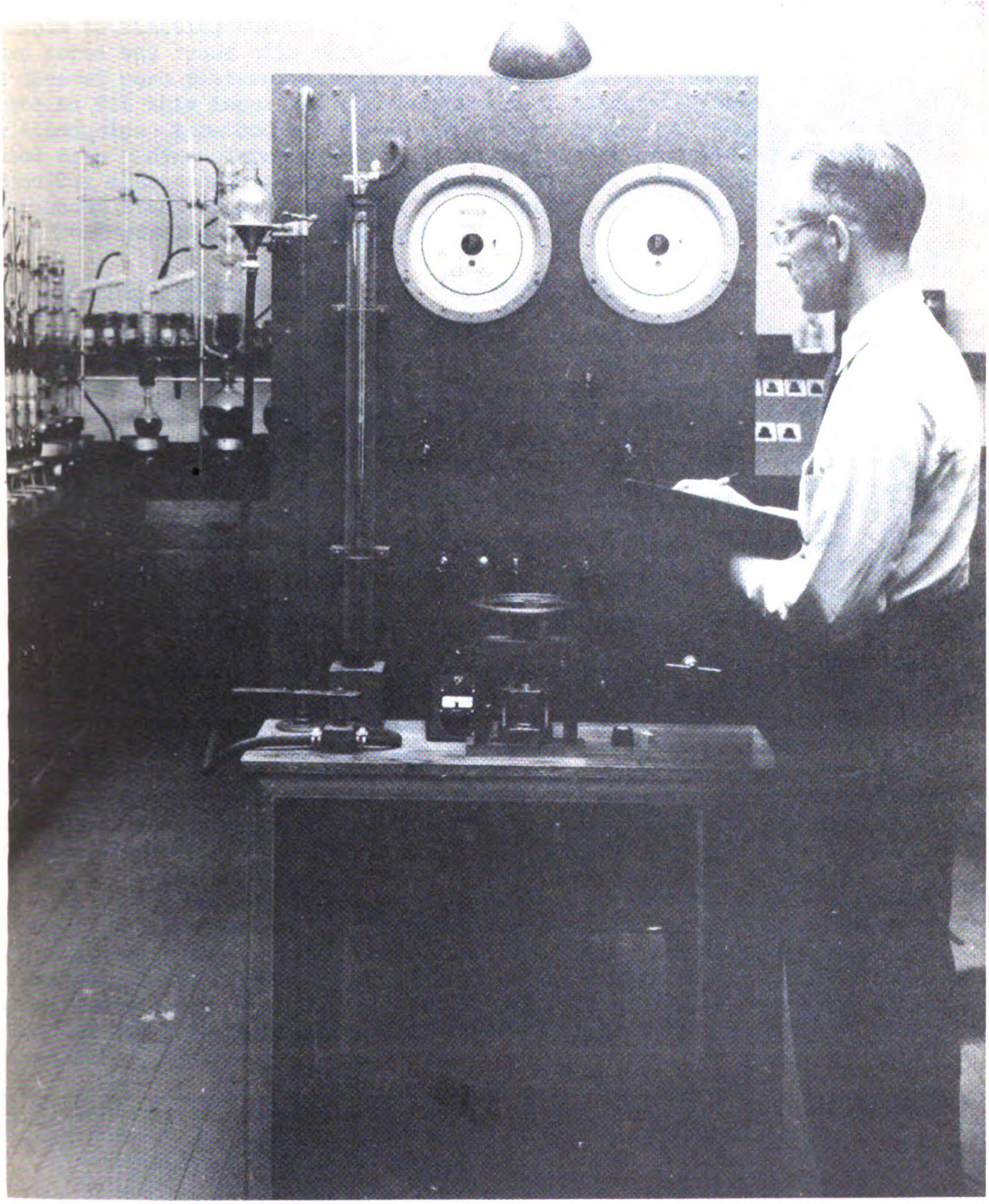

Figure 8. - Apparatus assembly for determining the permeability of specimens prepared from core samples of oil-producing formations.

flow tests was terminated when the produced air:oil ratio reached values comparable to limiting economic operations in practice. Several different rotary sand cores and crude oils were used in these investigations. Microscopy studies of pore patterns were conducted simultaneously with the flood pot tests to fit this important characteristic of sandstones into an oil recovery relationship. A method was developed whereby pieces of sandstone are impregnated with a dye-colored plastic and thin sections or polished surfaces prepared for microscopic examination and photography. The techniques for the microscopy study of pore patterns just reached a point at the end of the year where real results can be anticipated.

Gravitational Drainage of Oil from Unconsolidated Sands

Laboratory experiments started during World War II to determine whether additional oil could be obtained from a sand (after no more oil would drain to wells by gravity) by tunneling into the sand and applying heat at the exposed sand face to reduce the viscosity of the oil and cause some of the residual oil to drain to the excavated opening were concluded during 1948, and a report[19] was published. The experiment was carried out in a laboratory oil field consisting of a 3- by 3-foot box about 1 foot high packed with unconsolidated sand with 25 percent of the pore space filled with water and 75 percent with 13.1° A.P.I. gravity oil from the Kern River field, California. During the first part of the experiment, the oil drained from the sand through five wells, and 57 percent of the oil and 28 percent of the water originally added to the sand were recovered.

After no more oil drained from the reservoir through wells while the temperature of the sand body was maintained at 84° F., a tunnel was driven horizontally through the bottom of the sand body, and heating elements were installed. After applying heat in the tunnel for 75 days, during which time the temperature was increased progressively by 50° F. increments from 84° to 234° F., only slightly more than one-tenth of 1 percent of the oil remaining in the sand after gravitational drainage to wells at a temperature of 84° F. was recovered.

Failure of heat to increase oil recovery was attributed mainly to the caking of the sand about the tunnel as a result of the high temperatures maintained in the tunnel. Supplemental experiments are now underway to augment present knowledge of the effect of heat on the caking of oil sands. In these experiments, sands of different texture containing oils of different A.P.I. gravities are being used, so that the effect of heat upon a range of sands and oils will be explored.

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[19] Higgins, R. V., and Shea, G. B., Laboratory Studies of the Gravitational Drainage of Oil from Unconsolidated Sands: Bureau of Mines Rept. of Investigations 4391, 1949, 15 pp.

Fundamental Research

Nature of Surface Forces in Petroleum Reservoirs

A fundamental research program started late in 1948 is designed to provide a better understanding of the attractive forces between the solid, liquid, and gaseous phases in petroleum reservoirs. During the year a surface chemistry laboratory was equipped for this work, and the studies were started on three phases of the program - (1) surface phenomena at solid-fluid interfaces, (2) interfacial tension relationships between fluid interfaces, and (3) surface active extracts from crude petroleum.

The first project started was a basic study of the surface phenomena involved in the flow of single-phase fluids through packed sands. Instead of working with complex systems, this program is concerned with pure liquids and vapors and beds of carefully sized sands or powders of known purity, crystal structure, and surface properties. An apparatus has been developed for studying flow phenomena and for measuring the specific surface areas of fine sands and powders. Microscopic techniques have been developed which permit more accurate independent measurements of grain diameters and specific surface areas of sands, fine powders, and geological sediments.

Under the third phase of this study, an apparatus has been developed to extract surface-active substances from crude petroleum. In this equipment, water is slowly percolated through a tortuous glass column filled with crude oil, and it has been found that in the course of several weeks minute quantities of surface-active materials will be extracted from the oil and will collect at the oil-water interface in a receiver at the bottom of the column. This surface-active material then is subjected to organic chemical analysis by semi-micro techniques. If the nature of surface-active materials present in crude oils can be determined, it should be feasible to study certain reservoir flow phenomena, using systems wherein solutions of known molecular components would be substituted for crude petroleum. A research program on interfacial tension relationships of surface-active solutions has been instituted for this work.

Recovery of Hydrocarbons from Bituminous Sandstones

A report[20/] was published on the results of the Bureau's laboratory research in the adaptation of the hot-water separation process to the recovery of hydrocarbons from bituminous sandstones of the Edna deposit near San Luis Obispo, Calif. The report describes the construction and operation of the

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[20/] Shea, G. B., and Higgins, R. V., Laboratory Study of the Hot-water Process for Separating Hydrocarbons from Surface Deposits of Bituminous Sandstones Near Edna, Calif.: Bureau of Mines Rept. of Investigations 4246, 1948, 31 pp.

laboratory separation plant and discusses the problems involved and the results obtained in treating the Edna bituminous sandstones. The utilization of the recovered bitumen as a source of motor fuels, Diesel fuels, and fuel oils also is discussed, and data on cracking, analytical distillation, and its asphalt properties are summarized.

The studies demonstrated that the hot-water method of separation may be applied satisfactorily to separating hydrocarbons from the Edna sandstone, although the presence of mineral salts and fine sand in the deposits complicates the operation. The small-scale studies did not permit estimation of separation costs that might be expected in large-scale operations, but they did provide much information of a fundamental nature on the recovery of bitumen from oil-impregnated sandstones by the hot-water separation method.

Following the successful application of the hot-water separation process to the recovery of hydrocarbons from Edna sandstones, a series of tests on bituminous sandstones from the Vernal and Sunnyside, Utah, deposits showed that these sandstones also are amenable to treatment by the hot-water method of separation. The outcropping sandstones of Utah are reported to be the most extensive in the United States and contain some 2 or 3 billion barrels of oil.

PETROLEUM CHEMISTRY AND REFINING

The basic objective of chemistry and refining research is to provide comprehensive data on the composition of crude oil and its products, together with property data on the components. Such data are fundamental in the development of new refining methods, improvement of existing methods, and increasing efficiency of product utilization. The current program is discussed under the following five headings:

1. Crude oil evaluation.
2. Sulfur compounds in petroleum.
3. Composition of fuels and utilization characteristics.
4. Composition and properties of asphalt.
5. Gasoline surveys.

Crude Oil Evaluation

Routine-Type Analyses

One of the services that the Bureau of Mines has contributed to the petroleum industry is to provide the only public catalog of standardized crude-oil analyses extant. This service was initiated approximately 30 years ago and has been maintained since that time on a comparable basis, although modifications in keeping with industrial development have been made. It has proved of inestimable value to refiners, petroleum chemists, geologists, producers, and the National military establishment. Recently, because of increased imports of petroleum into the United States, crude oils from foreign countries have been included in the surveys. In addition to the studies relating to quality of the crude oils, some attention has been given to availability. During the current year the catalog has been maintained by the analysis of 111 crude oils distributed geographically as follows:

United States: Arkansas 2, California 10, Colorado 3
Michigan 2, Mississippi 3, Montana 2
New Mexico 3, Oklahoma 7, Pennsylvania 6
Texas 41, Utah 1, and Wyoming 22

Foreign: Alaska 1, Colombia 4, Greece 1, and Iran 3

Groups of analyses are published periodically. One such publication comprised a summary of the characteristics of Wyoming crude oils.[21] Complete analyses were given for two oils representative of low-sulfur and high-sulfur production in Wyoming, and summaries of analyses of 140 crude oils were tabulated.

Analysis at High Altitudes

Although the great majority of petroleum laboratories are at or near sea level, some - notably in the Rocky Mountain region - are at comparatively high altitudes. Consequently, analyses based on distillation at the lower atmospheric pressures are not comparable with those from sea-level laboratories. An apparatus has been developed[22] whereby the first distillation of the Bureau of Mines routine method can be run under pressure equal to that at sea level. Results are strictly comparable to those obtained at low altitudes.

Special Distillations for Motor and Aviation Gasoline, Jet Fuels, and Diesel Fuels

As a part of the over-all petroleum-supply picture, the Bureau has been procuring samples of foreign crude oils and analyzing them to determine their suitability for the manufacture of various types of fuels. The type of evaluation used for different crude oils was modified according to the type of crude oil, the amount of sample available, and the location of the oil field with relation to refining facilities. Superfractionation equipment is available at the Middle East Refineries, so naphthas prepared from ten crude oils from this area were superfractionated in a small laboratory unit. The fractions were analyzed for percentages of component hydrocarbons, using the refractometric method of Gooding, Adams, and Rall.[23] From these data, and the blending octane numbers reported by Schwartz, Gooding, and Eccleston[24] the octane numbers of the "isocuts" were calculated.

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[21] Ball, John S., and Espach, Ralph H., Crude Oils of Wyoming: The Petroleum Eng., vol. 20, No. 2, Nov. 1948, pp. 229-234.

[22] Wenger, Welton J., and Ball, John S., Analytical Distillation of Crude Oils at High Altitudes by the Bureau of Mines Routine Method: Bureau of Mines Rept. of Investigations 4517, 1949, 9 pp.

Superfractionation equipment is not available in South American refineries, so base stocks were prepared from the 21 crude oils available by distillation into wide-boiling cuts and then combining the maximum number of consecutive cuts that would make a 91 octane base stock with the addition of 4.6 ml. of TEL. In addition, a 5-gallon sample of each of the 31 South American and Middle East crude oils was distilled to provide the following fuels:

Fuel No.	Type fuel	Boiling range IBP	 90 percent
1	Jet fuel	100	550
2	Jet fuel	300	480
3	Diesel fuel	350	675

Inspection tests were made on each of the three fuels prepared from each crude oil.

A supplementary paper was prepared and published as a journal article[25] furthering the study presented in 1947 in the paper "High-Sulfur Crude Oils of the United States - Trends in Supply", by H. M. Smith and O. C. Blade. The additional data given in the article are summarized in table 1.

Sulfur Compounds in Petroleum

Ever since high-sulfur crude oil was discovered in Lima, Ohio, in 1885, sulfur compounds have presented problems to both refiners and consumers of petroleum and its products. During the last quarter century the Bureau of Mines has contributed toward the solution of some of these problems in several

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[23] Gooding, R. M., Adams, N. G., and Rall, H. T., Determination of Aromatics, Naphthenes, and Paraffins by Refractometric Methods: Ind. Eng. Chem., vol. 18, 1946, p. 2.

[24] Schwartz, F. G., Gooding, R. M., and Eccleston, B. H., Superfractionation Studies - Naphthas from Santa Barbara, Venezuela, Crude Oil: Ind. Eng. Chem., vol. 40, 1948, p. 2166.

[25] Blade, O. C., High-Sulfur Crude Oils - Trends in Supply. II. U. S. Data of 1945-47: Petroleum Refiner, vol. 28, March 1949, pp. 151-152.

TABLE 1. - Sulfur content and volume of crude-oil production in the United States from 1915 to 1947

Year	High sulfur (over 0.5 percent S)		Low sulfur (less than 0.5 percent S)		Ratio of high sulfur to low sulfur
	Millions of barrels	Percent of total U.S. production	Millions of barrels	Percent of total U.S. production	
1915	95	34	186	66	0.51
1920	144	33	299	67	.48
1925	339	44	425	56	.80
1930	382	43	516	57	.74
1935	295	30	702	70	.42
1940	444	33	909	67	.49
1945	600	35	1,114	65	.54
1946	608	35	1,125	65	.54
1947*	674	36	1,190	64	.57

* Subject to revision.

API RESEARCH PROJECT 48 A

SECTION ON SYNTHESIS & PURIFICATION OF SULFUR COMPOUNDS.

PETROLEUM & OIL SHALE EXPERIMENT STATION.
BUREAU OF MINES, LARAMIE WYOMING.

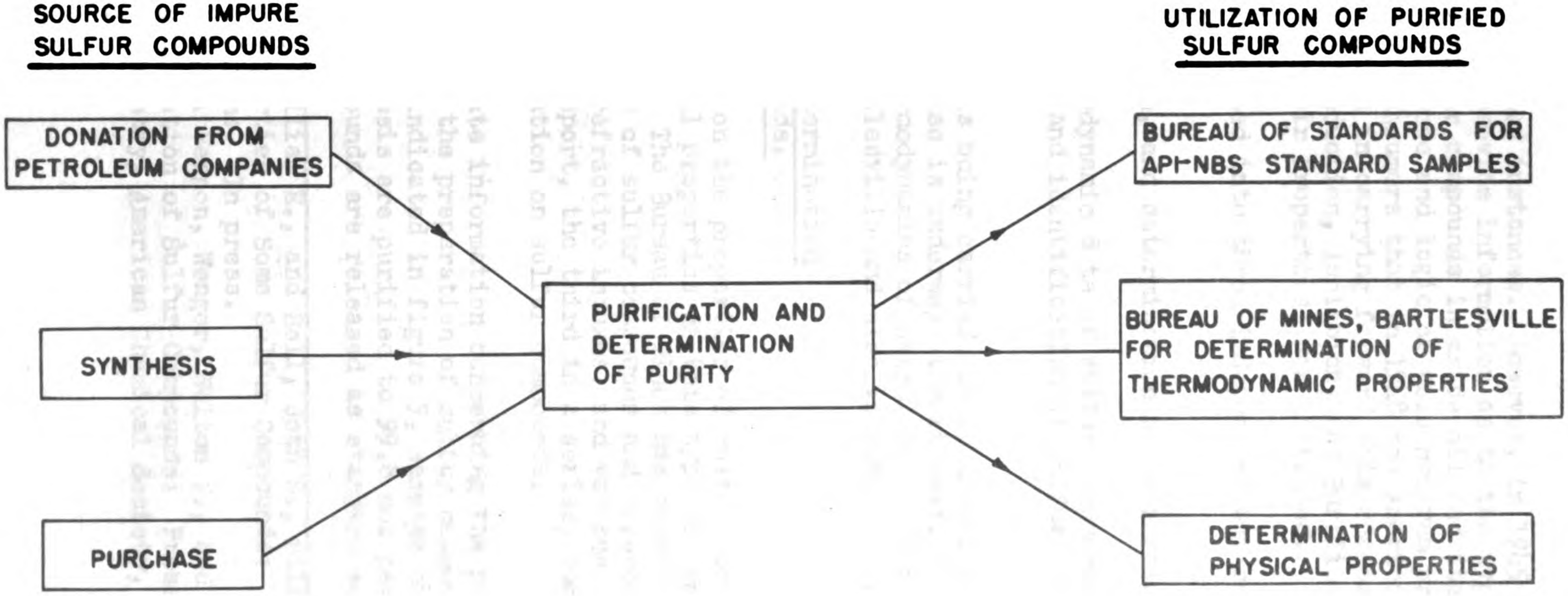
SOURCE OF IMPURE SULFUR COMPOUNDS
DONATION FROM PETROLEUM COMPANIES
SYNTHESIS
PURCHASE
PURIFICATION AND DETERMINATION OF PURITY
UTILIZATION OF PURIFIED SULFUR COMPOUNDS
BUREAU OF STANDARDS FOR API-NBS STANDARD SAMPLES
BUREAU OF MINES, BARTLESVILLE FOR DETERMINATION OF THERMODYNAMIC PROPERTIES
DETERMINATION OF PHYSICAL PROPERTIES

Figure 9. - Outline of work on synthesis, purification, and determination of properties of sulfur compounds.

specific but more or less isolated instances. However, in 1945 a carefully integrated program designed to provide information as to the type, quantities, and characteristics of the sulfur compounds in crude oil and its products was initiated by the Bureau. The scope and logic of this program promised to be of such value to refiners and consumers that in 1948 the American Petroleum Institute joined with the Bureau in carrying forward this research, and API Research Project 48A on "The Production, Isolation, and Purification of Sulfur Compounds and Measurement of their Properties" was initiated.

The research can be separated into three independent but related phases, which are:

1. Synthesis, purification, and determination of properties of sulfur compounds.
2. Determination of thermodynamic data of sulfur compounds.
3. Separation, isolation, and identification of sulfur compounds in crude oils.

The first of these phases is being carried out at Laramie, Wyo., and is discussed below. The second phase is underway at Bartlesville and is discussed under the section on thermodynamics of petroleum in this report. The third phase is conducted at Bartlesville and also is discussed below.

Synthesis, Purification, and Determination of Properties of Sulfur Compounds.

The need for reliable data on the properties of sulfur compounds has been shown by compilations of physical properties of this type of compound as obtained from published articles. The Bureau of Mines has continued its survey of the literature for properties of sulfur compounds and a report[26] giving viscosities, surface tensions, refractive indexes, and various calculated functions was prepared. This report, the third in a series, continues to show the gaps in the existing information on sulfur compounds.

To meet the need for accurate information concerning the properties of sulfur compounds, a program for the preparation of sulfur compounds in high purity has been developed. As indicated in figure 9, samples obtained either by donation, purchase, or synthesis are purified to 99.8 mol percent or better.[27] These purified compounds are released as standard samples for calibration of physical instruments through the National Bureau of Standards. The more common physical properties and spectral data are determined by the Bureau of Mines. The determination of their thermodynamic properties is carried out by another phase of API Project 48A.

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[26] Helm, R. Vernon, Haines, William E., and Ball, John S., Sulfur in Petroleum. III. Selected Properties of Some Sulfur Compounds: Bureau of Mines Rept. of Investigations. In press.

[27] Haines, William E., Helm, R. Vernon, Wenger, Welton J., and Ball, John S., The Preparation and Purification of Sulfur Compounds: Presented before Division of Petroleum Chemistry, American Chemical Society, San Francisco, Calif., Mar. 30, 1949.

In addition to the three compounds - thiophene, 2-thiabutane (methyl ethyl sulfide), and 3-thiapentane (diethyl sulfide) - which were purified last year and released as standard samples this year, four other compounds were purified. These are 1-pentanethiol, 2,3-dithiabutane (dimethyl disulfide), 2-methyl-2-propanethiol, and ethanethiol. An additional 10 compounds are in various stages of purification.

Synthesis has included the preparation of 1-pentanethiol (which has since become commercially available) and thiacyclopentane (tetrahydrothiophene). Exploratory preparations have been made of thiacyclobutane and 2-methylthiacyclopentane. Investigation of unsymmetrical disulfides gave the first reported[28] syntheses of 2,3-dithiapentane (methyl ethyl disulfide) and 3,4-dithiahexane (ethyl n-propyl disulfide).

The chief method of purification has been distillation, although other methods such as crystallization and chemical treatment have been used as occasion demanded. Many sulfur compounds have low decomposition temperatures, so that it has been necessary to make distillations at reduced pressures. The method developed by the National Bureau of Standards for determination of purity of hydrocarbons based on freezing-point measurements has been adapted for use with sulfur compounds. Purified compounds are bottled "in vacuum" in low-actinic glass ampoules to reduce possibility of change in composition.

Information concerning the temperature and reaction course for thermal decomposition of sulfur compounds is very scarce. A study has been started to augment existing data through the pyrolysis of certain sulfur compounds known to exist in petroleum. Progress to date has consisted in design of equipment and selection and development of methods of analysis.

Separation and Identification

In planning a study to separate, isolate, and identify sulfur compounds in crude oils it seemed important first to do some exploratory work regarding the distribution and types of sulfur compounds present in naphthas from a variety of sulfur-bearing crude oils. Toward this end, a scheme of analysis was developed whereby the crude oils selected for study were distilled, both at atmospheric pressure and at a pressure of one or two millimeters, taking fractions of equivalent volume in both instances. Group sulfur analyses were

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[28] Maticka, Jack B., Haines, William E., and Ball, John S., Unsymmetrical Disulfides - Occurrence and Preparation: Presented before Division of Petroleum Chemistry, American Chemical Society, San Francisco, Calif., March 30, 1949

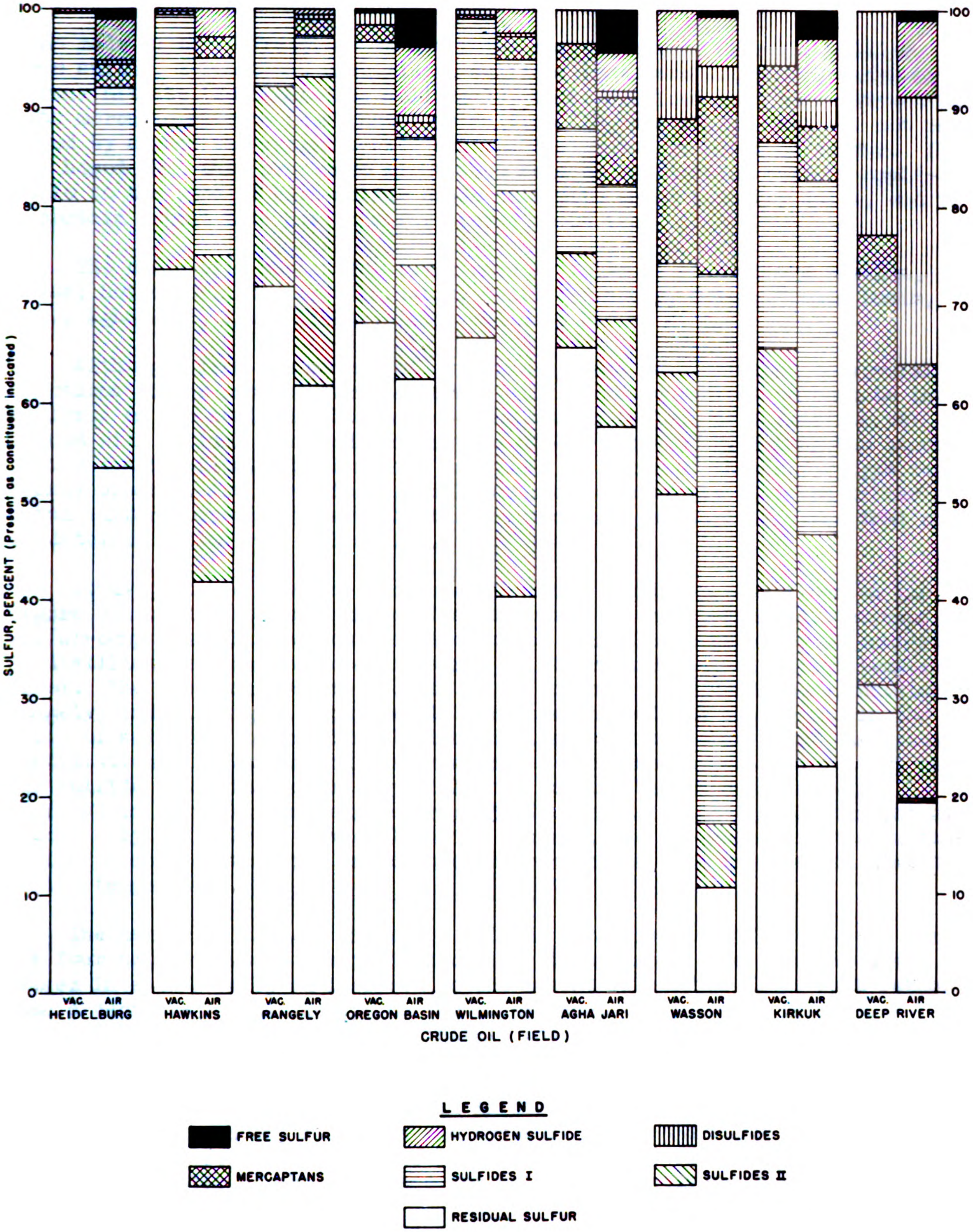

Figure 10. - Group sulfur analyses of crude oil naphthas.

then made on these fractions to determine the content of hydrogen sulfide, free sulfur, mercaptans, disulfides, sulfides that were extractable with mercurous nitrate (designated as sulfide I), those sulfides that were extractable with mercuric nitrate (designated as sulfide II), and sulfur that was not removed by any of the reagents used and was designated as residual sulfur. It was hoped that this procedure might show some classification pattern applicable to the type of high-sulfur crude oils with which industry deals, and to a certain extent this has thus far proved to be true.

The crude oils chosen for study were as follows: Wasson and Hawkins, Texas; Heidelberg, Miss.; Wilmington, Calif.; Rangely, Colo.; Oregon Basin, Wyo.; Agha Jari, Iran; Kirkuk, Iraq; and Deep River, Mich.

Although, from the method of experiment, data were obtained on several fractions of the naphtha for each crude oil, it is convenient to compute the analyses on the basis of the complete naphtha equivalent to a fraction obtained with a final overhead temperature of 480° to 485° F. during the atmospheric distillation. The computed analyses, in terms of the sulfur-type compounds present, are shown in figure 10 on the basis of the division of the total sulfur compounds present in the naphtha into the various types that can be determined plus residual sulfur.

Study of these data has indicated that the eight naphthas shown on the figure can be divided into three classes, based on the apparent differences in sulfur-compound behaviour on distillation at atmospheric pressure as compared to distillation under reduced pressure; in other words, at different temperatures. The important points seem to be as follows: (1) Heidelberg, Hawkins, Rangely, and Wilmington naphthas all decrease in residual sulfur and in the ratio of sulfide I to sulfide II with the increased temperature of atmospheric distillation; (2) Wasson and Kirkuk naphthas decrease in residual sulfur, but the sulfide ratio increases, especially so for the Wasson naphtha, with increase in distillation temperature; (3) Oregon Basin and Agha Jari naphthas change only slightly in residual-sulfur content, and the change in the sulfide ratios is smaller than for any of the other naphthas with increase in distillation temperature.

The manner of the change in the sulfide ratio is also of interest. For the four naphthas where the ratio decreases importantly, the decrease was caused in each case by an increase in the amount of sulfide II present rather than a decrease in sulfide I. On the other hand, the increase in sulfide ratio for Wasson and Kirkuk is definitely caused by an increase in the amount of sulfide I present.

The Deep River, Mich., crude oil is distinctly different from the other eight crude oils shown, so far as the types of sulfur compounds in the naphtha are concerned. It contains a very high proportion of mercaptans and disulfides in the ratio of about 2:1 and has only a relatively small amount of residual sulfur, less than 30 percent; although the residual sulfur decreases during distillation at atmospheric pressure, it does not appear as either sulfide I or sulfide II, but apparently as disulfides and hydrogen sulfide.

Composition of Fuels and Utilization Characteristics

Composition

Gasoline. - Superfractionation studies of naphthas from crude oils produced in the Middle East are of particular interest because refineries in that area have superfractionation equipment. Naphthas were prepared from 10 Middle East crude oils and superfractionated into small fractions in a laboratory unit. The compositions, in terms of individual hydrocarbons, were calculated by the method of Gooding, Adams, and Rall.[24]

A description of a special column head, designed and constructed for use in sample purification was published.[29]

Diesel fuels. - The problem of supplying the Diesel-engine operators with adequate supplies of high-grade fuel is of primary concern, not only to the refiner but also to the engine manufacturer. This interest is indicated by the number of organizations that are studying this problem through research programs and industry committees. The Bureau of Mines has recognized that one of the basic problems is the relationship between the composition of a Diesel fuel and its behavior in an engine. To this end the Bureau has formal or informal agreements with several of these organizations to supply basic data on the composition of fuels on which engine studies are being made.

One of these programs is with the Western Petroleum Refiners Association (WPRA), and it involves the preparation of Diesel fuels from several selected crude oils of different types that are representative of large production. The first fuel to be studied was prepared from West Edmond, Okla., crude oil, representative of midcontinent crude oils. The Diesel fuel was distilled into 134 fractions, the aromatics were separated from each fraction by silica gel adsorption, and the cetane numbers of the original fractions and the paraffin-naphthene portions of the fractions were determined.

From other physical properties, the composition, in terms of type hydrocarbons, was estimated for the paraffin-naphthene portion and the aromatic portion. The bargraph in figure 11 shows the estimated composition of the paraffin-naphthene portion plotted with the cetane number, and figure 12 shows the estimated composition of the aromatic portion.

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[29] Hopkins, R. L., Valveless Head Prevents Contamination or Other Failure in Distilling Columns: Petroleum Processing, vol. 4, No. 6, June 1949, p. 698.

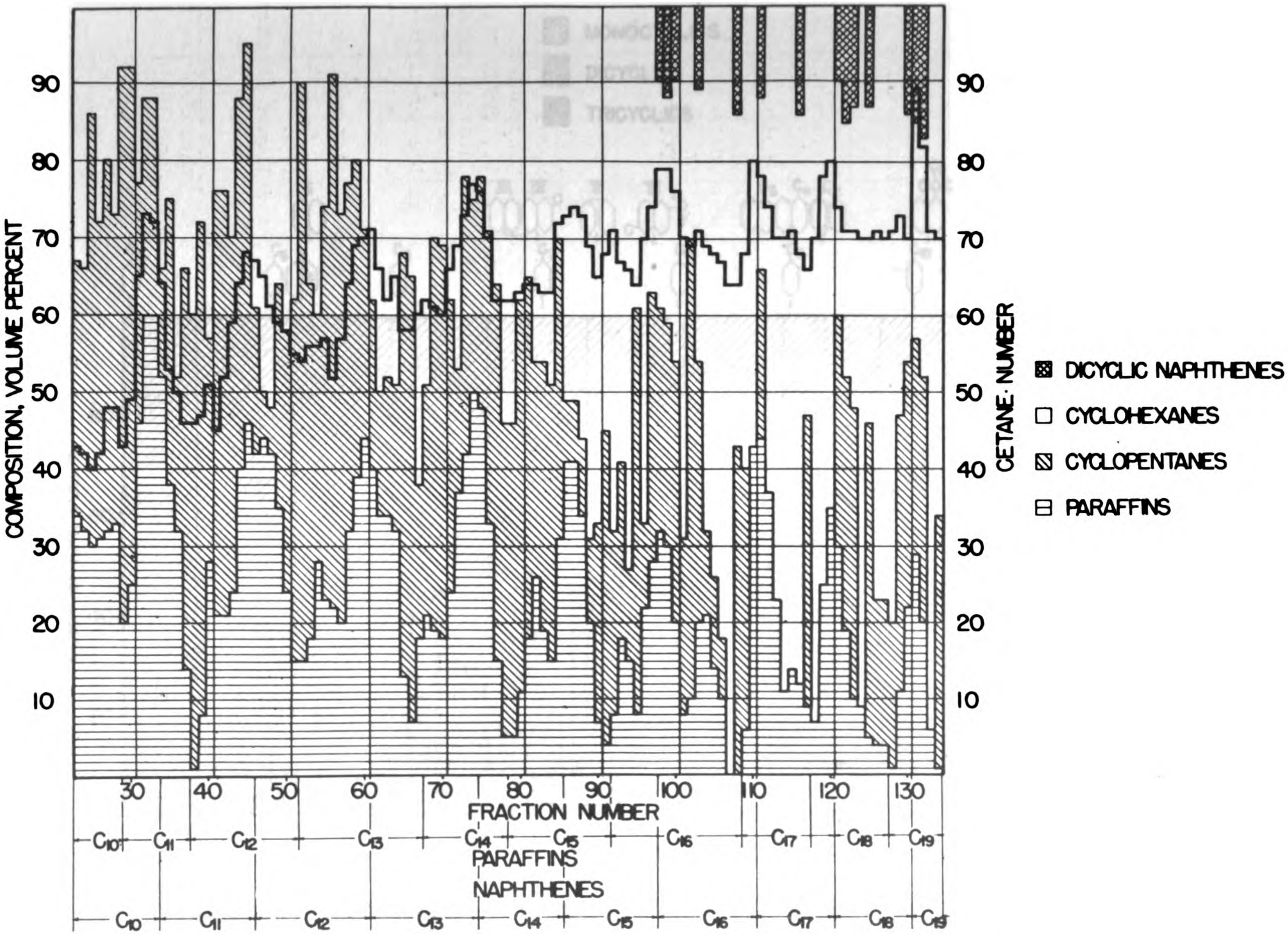

Figure 11. - Composition of paraffin-naphthene fractions of Diesel fuel from West Edmond crude oil.

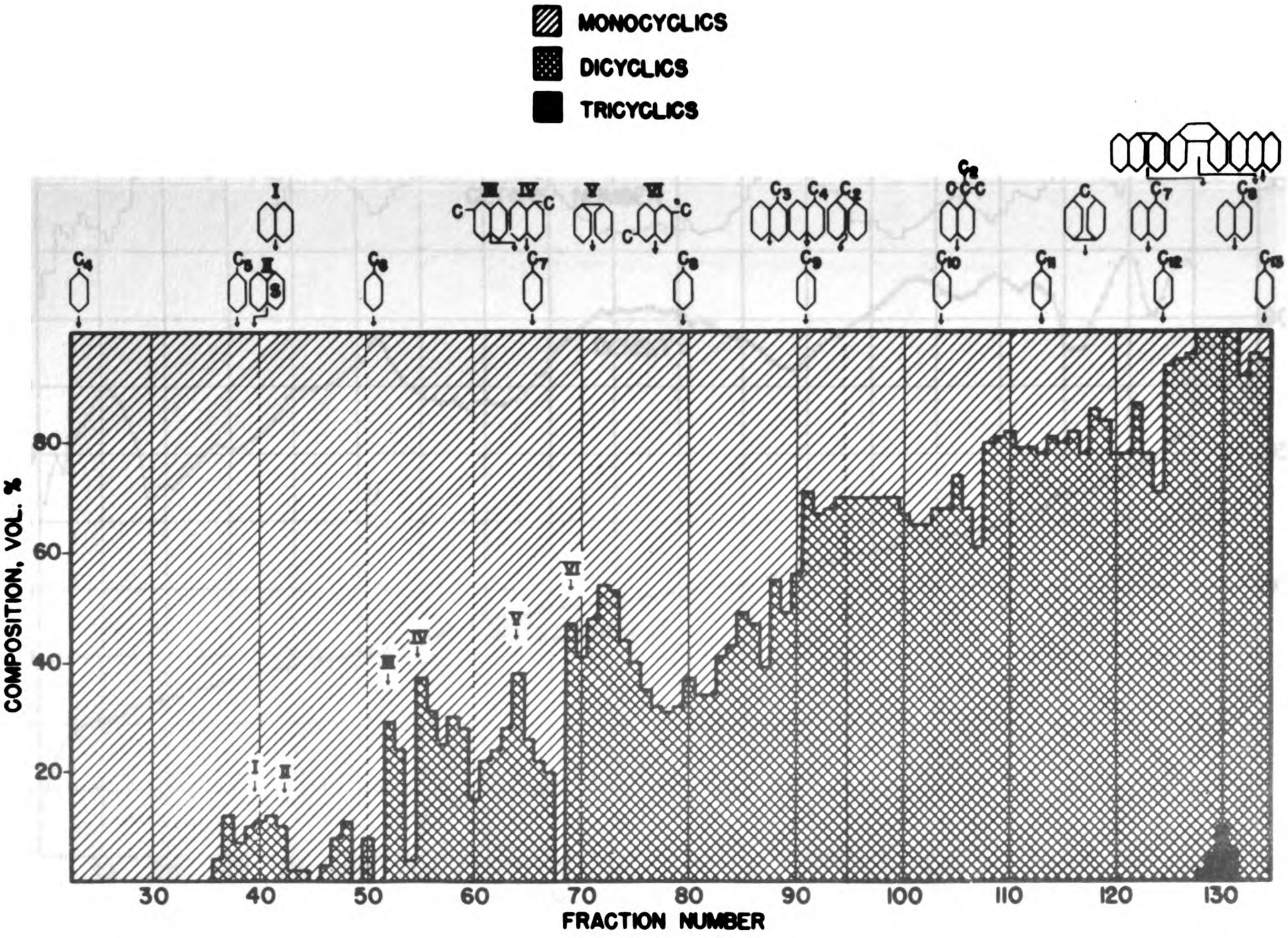

Figure 12. - Composition of aromatic fractions of Diesel fuel from West Edmond crude oil.

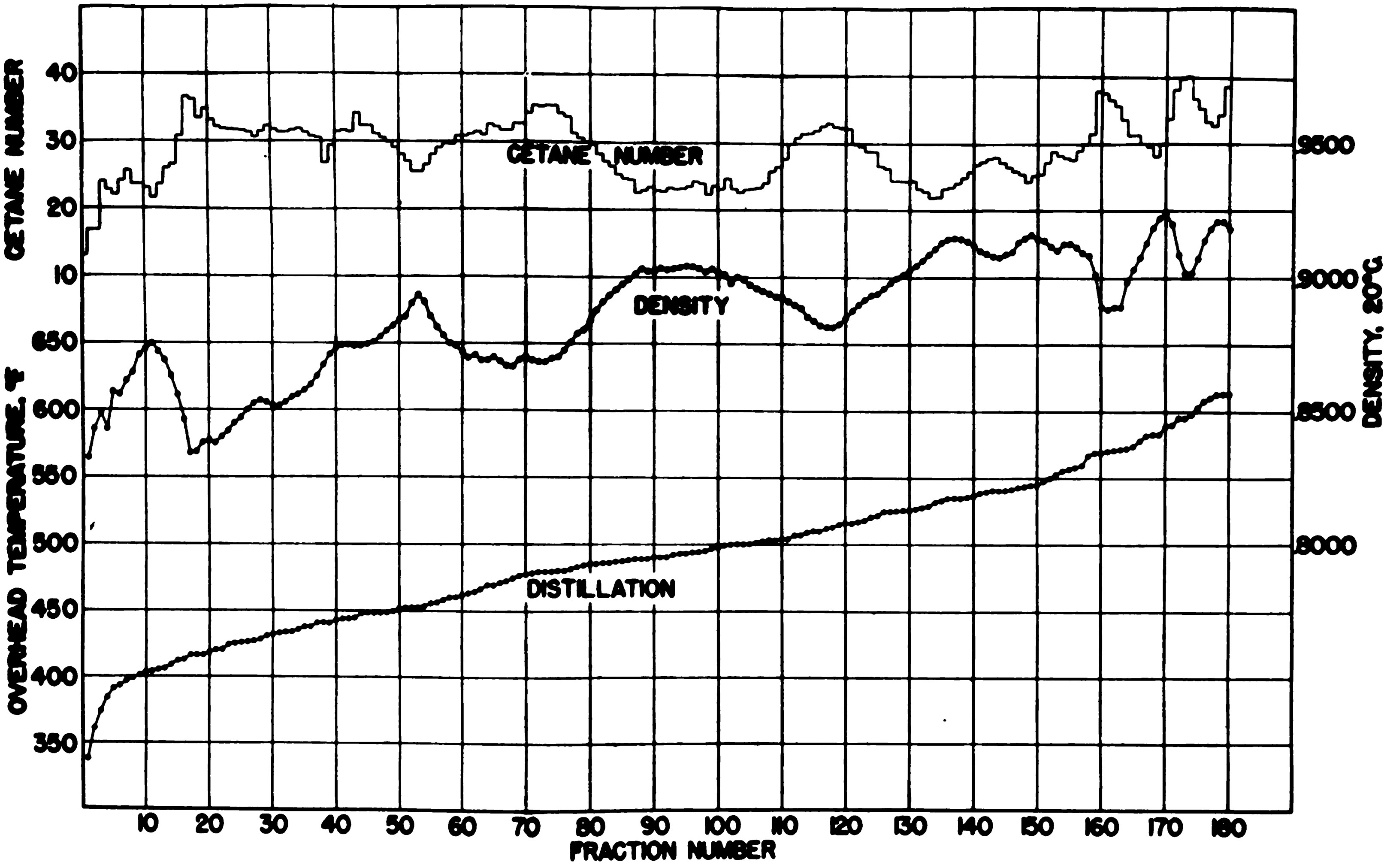

Figure 13. - Properties of fractions from catalytically cracked Diesel fuel.

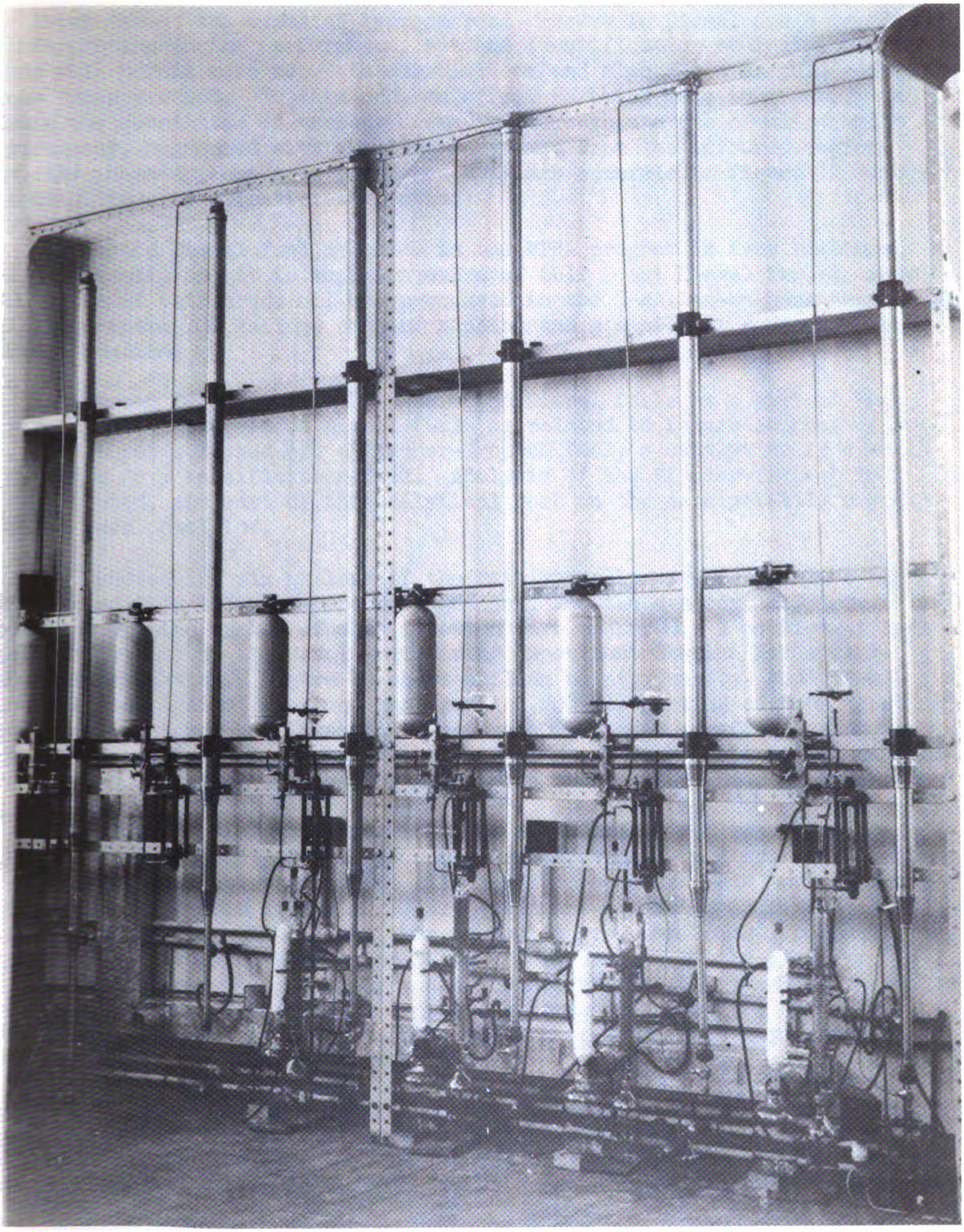

Figure 14. - Battery of six stainless-steel columns for separating hydrocarbon types of silica-gel adsorption.

Knowledge of the types of hydrocarbons present in Diesel fuels is helpful in interpreting engine performance, but the identification of individual compounds will permit more accurate correlations and also serve as guide posts as to the types present. To this end, an effort is being made to identify and measure the quantities of various aromatics through the use of ultraviolet spectroscopy, augmented with supplementary data from the infrared region. Thus, the aromatic compounds indicated by Roman numerals in figure 12 have been identified by ultraviolet spectra.

The second Diesel fuel selected in the WPRA program is from Hastings, Tex., crude oil, and it is representative of Gulf Coast Diesel fuels. About 700 gallons of this crude oil was processed in the 5-gallon-an-hour continuous still to prepare 100 gallons each of naphtha and gas oil for subsequent composition studies.

The Bureau is analyzing three selected Diesel fuels as a part of the Navy's extensive program on Diesel fuels as related to future sources of supply. The three selected are a Fischer-Tropsch fuel, a catalytically cracked fuel, and a Navy specification fuel. Analysis of the Fischer-Tropsch fuel has been completed, and most of the analytical work on the catalytically cracked fuel has been completed.

One hundred and six gallons of the catalytically cracked fuel was superfractionated into 180 half-percent fractions, and the density, refractive index, and bromine number of each fraction were measured. A portion of each fraction was sent to the Naval Engineering Experiment Station for cetane-number determination. Figure 13 shows boiling point, density, and cetane number plotted against fraction number. A 1,200-ml. portion of each fraction was percolated through silica gel to separate it into a paraffin-naphthene and an aromatic portion. Properties were determined on each portion, and samples were sent to the Naval Engineering Experiment Station for cetane numbers.

The percentages of aromatics in these fractions were higher than in straight-run fractions, and it was necessary to design and construct a battery of stainless-steel columns for the silica-gel separations made in this study. These columns and some of the auxiliary equipment are shown in figure 14. The photograph shows the six columns, sample containers, manifolds, flow-metering apparatus, and four solvent strippers in the lower part of the picture. To the left, not shown in this figure, are the solvent storage tanks and services supply. Nitrogen under pressure is used to force solvents from the tanks through the columns. Steam is used to heat the solvent strippers, and ice water condenses the solvent vapor.

To get good separation in the Diesel fuel-boiling range, it is necessary to use a solvent, or "spacer," such as pentane between the sample and the desorbent, and this solvent must be removed by distillation from the sample after treatment. The usual practice is by a batch distillation. However, in this investigation a continuous steam-heated stripper was designed and constructed for each column. In this way the solvent was removed continuously during operation and resulted in the saving of many hours.

It is of interest to note the quantities of materials required for the silica-gel treatment of the 180 fractions:

Materials used	Quantity
Silica gel	1 ton
Isopropyl alcohol	270 gal.
Acetone	135 gal.
n-Pentane	30 gal.
Benzene	10 gal.

Some incidental observations indicated oxidation of certain Diesel-fuel fractions with an accompanying increase in cetane number. When plans were made to study the catalytically cracked fuel it became important to know whether peroxides were present and, if so, their effect on cetane number. Therefore, a program was planned to evaluate the effect of selected peroxides on cetane number, to select a satisfactory means of analyzing for peroxides, and to find a means of inhibiting peroxide formation. The increase in cetane number resulting from the addition of di-tertiary butyl peroxide and tetralin hydroperoxide to peroxide-free base stock is shown in the following table.

Di-tertiary butyl peroxide		Tetralin hydroperoxide	
Percent	Cetane number increase	Percent	Cetane number increase
0.5	11	0.5	5
1.0	18	1.0	8
		2.0	14

These data resulted in the decision to inhibit all fractions from silica gel treatment immediately after preparation. n,n'-Disecondary butyl para phenylene diamine was found to be an effective oxidation inhibitor in a concentration of approximately 0.01 gm./liter.

Jet fuels. - The increasing importance of jet propulsion for military aircraft has resulted in considerable emphasis on investigation of physical and chemical properties of jet engine fuels and the relationship of such properties to performance tests. Ten jet-propulsion fuels were analyzed by the Bartlesville laboratory, as a laboratory member of the Panel on Laboratory Tests on Turbine Fuels, Civil Aircraft Fuels Performance Group, Coordinating Research Council. In addition to the routine analyses, special analytical equipment and methods were devised for determining extremely small amounts of moisture in the samples.

Utilization

A necessary corollary to fuel-composition studies are utilization studies on the combustion characteristics of the fuel in an engine. In order better to interpret fuel composition in terms of utilization, the Bureau is approaching the problem of combustion by continuing its efforts to improve the precision of engine testing and by making studies of fundamental combustion characteristics in a constant-volume combustion bomb.

Engine testing. - The engine laboratory has continued active participation in national and local exchange sample-testing activities. As leader of a local group, a member of the staff maintains close liaison between national and local ASTM activities. In this manner the Bureau and other local laboratories have kept abreast with and contributed materially to the further refinement of test techniques.

Two aviation-fuel test engines, one motor-fuel test engine, and one Diesel-fuel test engine have been employed continuously throughout the year in routine rating of samples processed by the Bureau, in rating of exchange samples, in calibrating reference fuels used throughout industry, and in conducting special engine combustion schedules. Early in 1949 the Bartlesville laboratory was instrumental in detecting and calling attention to a deterioration of Diesel reference fuel that was adversely affecting the accuracy of Diesel-fuel testing throughout the Nation. Special investigations of fuel combustion in the CFR Diesel engine have more clearly defined the range of dependability of this test unit.

Fundamental studies. - Experimental studies of the fundamental combustion phenomena were intensified through the development of a constant-volume combustion-bomb and associated instrumentation. This test apparatus, completed in late 1948, effects a single injection of fuel into an air-charged, heated reactor; the injection process and ensuing pressure testing are portrayed on and photographed from a cathode-ray screen. This equipment holds promise as a tool for obtaining fundamental information on the combustion behavior of different fuels under various operating conditions.

Keen interest in these fundamental studies is displayed by many representatives of the engine and petroleum industries and by the military. The Coordinating Research Council provided substantial financial support in 1949.

The initial phase of testing the apparatus, involving tests of several fuels over wide pressure-temperature ranges, was completed in the first half of 1949. Consideration of engine tests to correlate with the bomb tests has paralleled the bomb investigations. Instrumentation has been designed and is being constructed to give engine data comparable to those obtained from the bomb-combustion records.

Inasmuch as auto-ignition of fuels outside an engine has been given relatively little attention, this project has brought forth many new problems, but it also holds great potentialities. The primary problem is being given much study while testing, development, and evaluation of the constant-volume combustion apparatus is continued.

Composition and Properties of Asphalts

A survey was completed concerning the yields and properties of straight-run asphalts from Rocky Mountain crude oils in comparison with asphalts from representative crude oils of California, Arkansas, and Mexico. The properties of the asphalts from 20 different crude oils of Wyoming and Montana indicated that these asphalts could be used for those commercial applications for which the asphalts of the California, Arkansas, and Mexico crude oils are satisfactory. Series of asphalts of different consistency were also prepared from a native bitumen of Rozel Point, Utah, and from oils extracted from bituminous sandstones of the Edna deposit in San Luis Obispo County, Calif., and the Athabaska deposit in Alberta, Canada. Although these asphalts differed from straight-run petroleum asphalts in several respects, their properties, as determined by common asphalt tests, indicated they could be used for some of the same purposes as petroleum asphalts. Manuscripts for two reports describing this work were completed, and the publications should be available soon.[30] [31] A laboratory drying oven and the extraction apparatus used in these studies are shown in figure 15.

The inability of standard asphalt tests to detect or account for certain variations in the properties of asphalts prepared by different methods or obtained from different sources indicates a need for more fundamental information concerning the constitution of asphalts. An analytical method was developed[32] to separate asphalt quantitatively into three groups of constituents, and a study was started to determine the properties of the asphalt constituents. Development of a suitable method of separating asphalt into three or more groups of constituents in sufficient quantity for further analysis is now in progress. One of the difficulties encountered in this separation was the procurement of a satisfactory adsorbent for the removal of resinous material. It was found that different batches of the anhydrous alumina formerly used in asphalt analyses had different adsorption characteristics; accordingly, a study is being made to prepare an alumina adsorbent having constant and reproducible adsorption characteristics.

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[30] Stanfield, K. E., and Hubbard, R. L., Asphalts from Rocky Mountain Crude Oils, Laboratory Preparation and Comparison: Bureau of Mines Tech. Paper 717. In press.

[31] Hubbard, Rethel L., and Stanfield, K. E., Laboratory Study of Asphalts from Native Bitumens and Bituminous Sandstones: Bureau of Mines Rept. of Investigations 4523, 1949, 22 pp.

[32] Hubbard, Rethel L., and Stanfield, K. E., Determination of Asphaltenes, Oils, and Resins in Asphalt: Anal. Chem., vol. 20, 1948, p. 460.

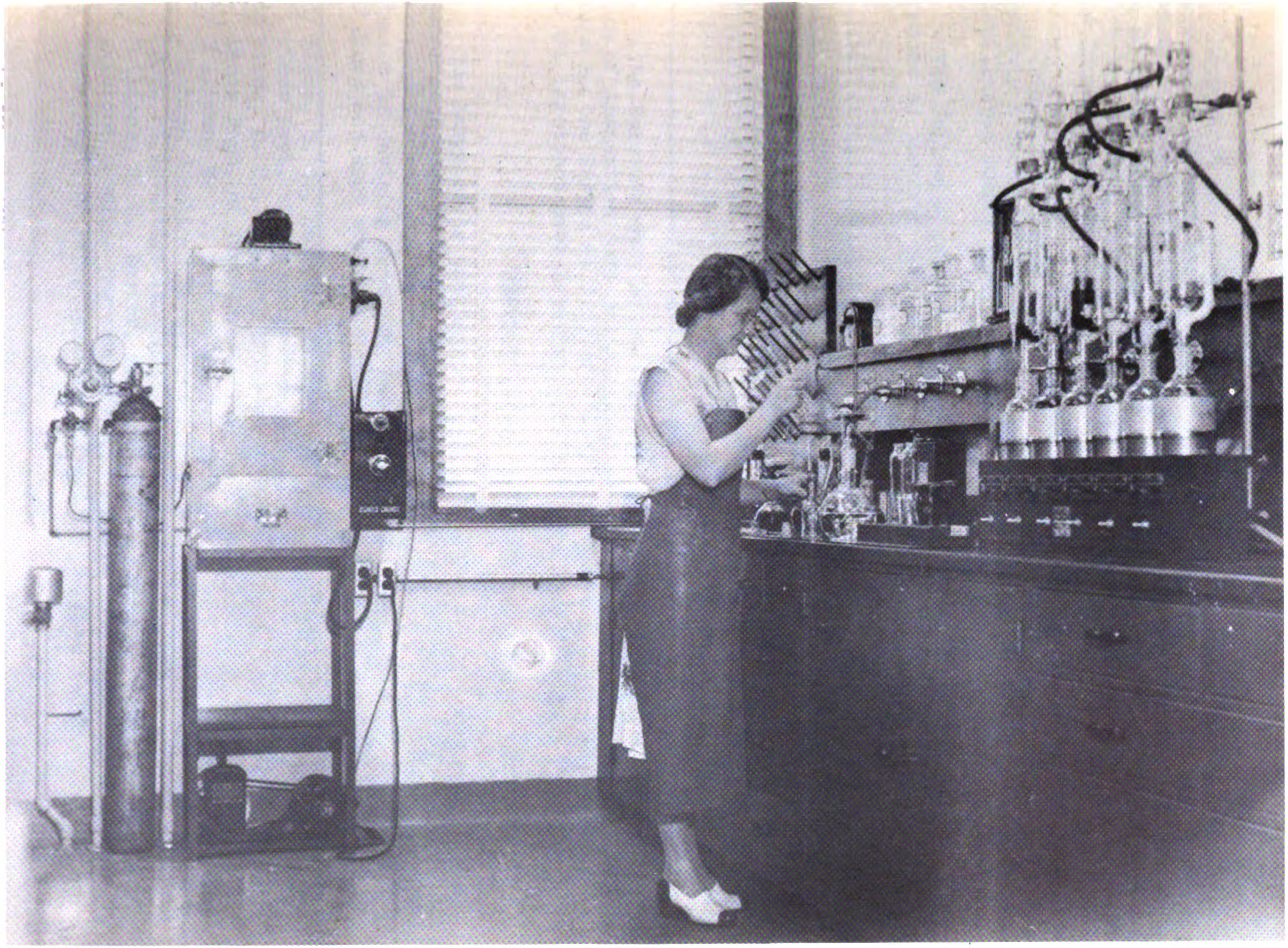

Figure 15. - Asphalt laboratory, showing drying oven and extraction apparatus.

Gasoline Surveys

Reports of two motor gasoline surveys[33/] [34/] and two aviation gasoline surveys[35/] [36/] were published during the fiscal year as a means of keeping the consumer, petroleum refiner, and engine manufacturer informed of the quality of gasolines being sold. The motor gasoline surveys were made in cooperation with the American Petroleum Institute, and the aviation gasoline surveys with the Coordinating Research Council.

Compared with last year's surveys the octane numbers of motor gasoline indicate a continued upward trend, vapor pressures are somewhat higher, and distillation ranges show only small changes.

The following tabulation shows the average national motor method octane numbers as compared with those for the two previous years:

Grade of gasoline	Fiscal year 1947		Fiscal year 1948		Fiscal year 1949	
	Summer, 1946	Winter, 1946-47	Summer, 1947	Winter, 1947-48	Summer, 1948	Winter, 1948-49
Premium price . . .	78.3	78.5	79.2	79.4	79.5	79.7
Regular price . . .	74.4	75.0	75.1	75.3	75.2	75.6

The Bureau's work in the aviation gasoline surveys involves the compilation of inspection data determined by the manufacturer and special data determined by the Bureau on factors affecting vapor lock. Table 2 summarizes some of the important data from the last three surveys.

THERMODYNAMICS OF PETROLEUM

The large-scale manufacture of useful products from petroleum has continued each year to become more nearly an exact science. This has increased the need for reliable thermodynamic data that can be used by the engineer and chemist in devising processes and planning manufacturing plants. The Bureau of Mines has kept abreast of the times by maintaining a continuous flow of

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33/ Blade, O. C., National Motor-Gasoline Survey, Summer 1948: Bureau of Mines Rept. of Investigations 4444, 1948, 33 pp., 3 figs.

34/ Blade, O. C., National Motor-Gasoline Survey, Winter 1948-49: Bureau of Mines Rept. of Investigations 4567, 1949, 33 pp., 3 figs.

35/ Holliman, W. C., Barker, M. G., Bobrowski, Nancy, Survey of Commercial Aviation Gasoline Characteristics - July 1948 Production: Bureau of Mines Rept. of Investigations 4435, 1948, 17 pp., 7 figs.

36/ Holliman, W. C., Barker, M. G., Bobrowski, Nancy, Survey of Commercial Aviation Gasoline Characteristics - January 1949 Production: Bureau of Mines Rept. of Investigations 4529, 1949, 17 pp., 7 figs.

TABLE 2. - Summary of aviation gasoline survey data

Test	Grade 80			Grade 91/98			Grade 100/130			Grade 115/145		
	Jan. 1948	July 1948	Jan. 1949	Jan. 1948	July 1948	Jan. 1949	Jan. 1948	July 1948	Jan. 1949	Jan. 1948	July 1948	Jan. 1949
Octane No.:												
Lean mixture	80.3	80.7	80.5	92.8	93.4	93.3	iso+ 0.13	iso+ 0.13	iso+ 0.11	-	-	-
Rich mixture	-	-	-	98.6	98.8	98.6	-	-	-	-	-	-
Performance No.:												
Lean mixture	-	-	-	-	-	-	105.1	104.8	104.5	117.6	116.7	118.8
Rich mixture	-	-	-	-	-	-	130.7	130.6	131.1	145.8	146.2	146.2
RVP, pounds	6.6	6.3	6.2	6.5	6.5	6.4	6.5	6.4	6.3	6.5	6.4	6.3
D-86 dist. temp., °F.:												
90% evaporation . .	236	236	239	233	236	237	244	245	246	250	243	242
Sum 10+50	336	341	343	341	340	342	350	350	350	356	364	360
Sp. gr., 60°/60° F. . . .	.706	.707	.707	.712	.711	.712	.704	.706	.708	.700	.701	.697
Viscosity, kinematic, 70° F., cs.	.592	.594	.595	.592	.591	.592	.605	.604	.601	.606	.619	.616

accurate and reliable thermodynamic data for hydrocarbons and other compounds that are of interest to the industry. During the past year an intensive systematic study of the thermodynamic properties of sulfur compounds was initiated in collaboration with the American Petroleum Institute.

The work is discussed under appropriate subheadings in the following paragraphs.

Low-Temperature Calorimetry

The thermal data obtained at low temperatures permit calculation of the fundamental thermodynamic property known as entropy, which is essential for the evaluation of yields from chemical processes.

During the year a number of compounds were investigated over the temperature range 11° Kelvin (-440° F.) to room temperature and higher. The results of these investigations were made available to those interested through publication in API tables, journal articles, and in papers presented before scientific meetings.

The results of a careful study of the low-temperature thermal properties of a complete series of hydrocarbon isomers[37] was published in the leading chemical journal. In another investigation the thermal properties of cyclopentene and cyclohexene[38] were determined.

Certain properties of the very interesting and important material cyclooctatetraene[39] also were determined. This compound is of potential use as an intermediate in many chemical processes. In conjunction with the API sulfur program, a comprehensive study of the thermodynamic properties of thiophene[40] was completed, and additional work was done on three other compounds, namely thiabutane, 3-thiapentane, and 2,3-dithiabutane.

37/ Huffman, H. M., Todd, S. S., and Oliver, G. D., Low-Temperature Thermal Data on Eight C_8H_{16} Alkylcyclohexanes: Jour. Am. Chem. Soc., vol. 71, 1949, p. 584.

38/ Huffman, H. M., Eaton, M., and Oliver, G. D., The Heat Capacities, Heats of Transition, Heats of Fusion, and Entropies of Cyclopentene and Cyclohexene: Jour. Am. Chem. Soc., vol. 70, 1948, p. 2911.

39/ Scott, D. W., Gross, M. E., Oliver, G. D., and Huffman, H. M., Cyclooctatetraene; Low Temperature Heat Capacity, Heat of Fusion, Heat of Vaporization, Vapor Pressure and Entropy: Jour. Am. Chem. Soc., vol. 71, 1949, p. 1634.

40/ Waddington, G., Knowlton, J. W., Scott, D. W., Oliver, G. D., Todd, S. S., Hubbard, W. N., Smith, J. C., and Huffman, H. M., Thermodynamic Properties of Thiophene: Jour. Am. Chem. Soc., vol. 71, 1949, p. 797.

Vapor-Heat Capacity and Heats of Vaporization

In order to extend the usefulness of the thermodynamic data, studies also were made of the heat of vaporization and vapor-heat capacity. These data, when combined with those obtained on solids and liquids, permit the computation of thermodynamic properties in the gas phase. Studies were made of the heat of vaporization and vapor-heat capacity of thiophene[22/] and additional compounds such as spiropentane, isopentane, carbon bisulfide, and others (the results of which have not as yet been published). A very interesting and useful byproduct of these studies is the obtaining of information about gas imperfection, which is necessary to predict the behavior of real gases. This phase of the investigation was discussed before the American Chemical Society.[41/]

Combustion Calorimetry

The data obtained in these studies are of fundamental importance in obtaining the heat of reaction required for the solution of many problems.

Work was continued on the very complex problems of obtaining heats of combustion of compounds containing sulfur and chlorine as well as on simpler materials. The heat of combustion of thiophene[40/] was measured, and improvements in the technique for combustion of chloro compounds[42/] were made. Other measurements[43/] were made on 2,2' -bis (4-hydroxyphenyl) propane, a compound of industrial importance.

Vapor Pressure

A knowledge of this property is useful in a number of ways. For example, the data may be used to calculate heats of vaporization. The compounds that have been studied include thiophene,[40/] cyclooctatetraene,[39/] hydrazine,[44/] and others.

[41/] Waddington, Guy, Gas Imperfections of Some Hydrocarbons and Derivatives: Abstracts of Papers, 114th meeting, American Chem. Soc., Portland, Ore., Sept. 1948.

[42/] Hubbard, W. N., and Huffman, H. M., The Heats of Combustion of o- and m-Dichlorobenzene. Further Improvements in the Combustion Technique: Abstracts of Papers, 115th meeting, American Chem. Soc., San Francisco, Calif., March 1949.

[43/] Hubbard, W. N., Knowlton, J. W., and Huffman, H. M., The Heat of Combustion of 2,2' -bis (4-hydroxyphenyl) propane: Jour. Am. Chem. Soc., vol. 70, 1948, p. 3259.

[44/] Scott, D. W., Oliver, G. D., Gross, M. E., Hubbard, W. N., and Huffman, H. M., The Entropy of Hydrazine. The Possibility of Random Orientation in the Solid: Abstracts of Papers, 114th meeting, American Chem. Soc., Portland, Ore., Sept. 1948; published in Jour. Am. Chem. Soc., vol. 71, 1949, p. 2293, entitled: Hydrazine: Heat Capacity, Heats of Fusion and Vaporization, Vapor Pressure, Entropy, and Thermodynamic Functions.

Statistical Mechanical Calculations

This powerful tool has been used to extend the experimental data into temperature regions which were impracticable by experimental methods. In particular, data were obtained on the compound hydrazine,[44] which is of considerable interest because of its potential use as a rocket fuel. Similar extensions of experimental data were also made for thiophene[41] and other compounds.

Summary

The thermodynamics research group has continued to supply engineers and research workers with a steady flow of reliable thermodynamic data. Cooperation has been maintained between this research group and industrial, university and Government laboratories. The experimental data have been extended by use of supplementary tools and have been made available promptly to interested persons and groups through publication and correspondence.

TRANSPORTATION OF NATURAL GAS

Natural Gas Hydrates

The Bureau of Mines, in cooperation with the American Gas Association, during several years just prior to World War II conducted a study of natural-gas hydrates, solid, icelike compounds that under certain conditions form in high-pressure natural-gas pipe lines at temperatures well above the freezing point of water. Enough of these solid compounds may accumulate to obstruct completely the flow of gas in the lines, thus preventing delivery of gas at times when it may be urgently needed and imposing costly remedial measures to remove the obstruction and put the lines back into operation. The study was discontinued during the war but subsequently was reactivated to the extent of reviewing and appraising the former work and preparing a comprehensive summary report. This report was published in November 1948 as Bureau of Mines Monograph 8.[45] The demand for the publication was so great that a second printing was necessary in March 1949. The monograph furnishes information needed by the natural-gas industry in understanding the nature of gas hydrates, avoiding difficulties resulting from hydrate formation, and providing a handbook on the subject for use of the natural-gas industry.

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[45] Deaton, W. M., and Frost, E. M., Jr., Gas Hydrates and Their Relation to the Operation of Natural-Gas Pipe Lines: Bureau of Mines Mono. 8, Published by the American Gas Association. (Available from the American Gas Association, 420 Lexington Avenue, New York 17, N. Y., at $1.50 per copy).

A problem of much interest to the natural-gas industry in transporting gas long distances in cross-country pipe lines is the removal of water from the gas entering the lines. During the Bureau's study of natural-gas hydrates, it was observed that condensed water in the pipe lines was a necessary factor in the formation of gas hydrates and resulting difficulties. The common practice is to dehydrate the gas to such an extent that there will be no chance of water condensing in the line. The value of a convenient, reliable means of continuously determining the water-vapor content of the gas is obvious.

As a result of the Bureau's study, an electrically operated and relatively simple recorder has been developed, which gives good promise of fulfilling the industry's need. One of the instruments has undergone extensive tests on natural-gas pipe lines. It has been in continuous operation since January 7, 1949, on pipe lines operating at pressures of 400 to 700 p.s.i. It is calibrated directly in water dewpoint temperatures that generally are most useful to the pipe-line operators, but it could be calibrated directly in water-vapor content if such information were more usable.

Flow of Natural Gas in Pipe Lines

The flow of natural gas in pipe lines is being studied. This research project, conducted in cooperation with the American Gas Association, has as its objective the development of an accurate formula for predicting or gaging the performance of high-pressure natural-gas pipe lines. The major uncertainty in present formulae is in the coefficient of friction involved in the flow of gas through pipes.

The project is divided into four broad phases involving (1) library review, (2) laboratory research, (3) field research, and (4) development of conclusions from the experimentation. Library research is substantially complete. Experimental flow tests with 2-inch, commercial, seamless, steel pipe were virtually finished during the past fiscal year. The results showed good correlation between the coefficient of friction and the rate of flow, the probable error being less than 1 percent. The results to date do not agree with any published equation so far advocated by others.

The rather startling discovery was made that there is a significant difference in the friction of flow in the 2-inch pipe, depending on the direction of flow. This fact must be explored further to determine, if possible, the pipe characteristics that cause such variation.

In order to evaluate the effect of pipe roughness and other deviations from idealized cylindrical shape, a 3-inch, superfinished, stainless-steel, experimental pipe line 122 feet long was fabricated. The machine work, performed at the Naval Gun Factory in Washington, D. C., resulted in what is probably the closest approach ever made to a true geometrical cylinder of

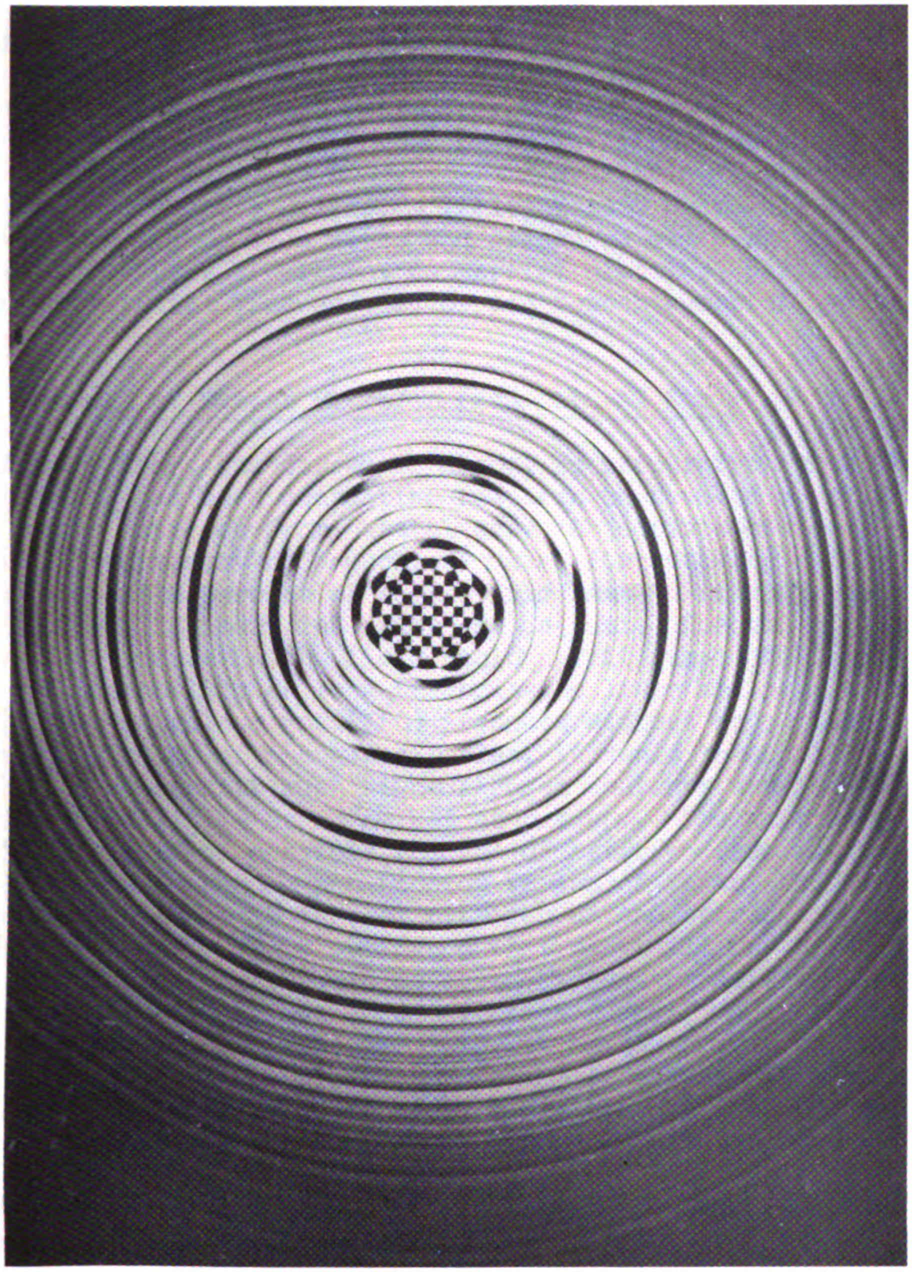

Figure 16. - Reflection of geometrical pattern in mirror finish of 3-inch super-smooth experimental pipe.

appreciable length. Tests over a wide range of "Reynolds numbers" are expected to furnish a "yardstick" for comparing and gaging the performance of ordinary pipe. The reflection of a geometrical pattern in the inside mirror finish of the super-smooth pipe is shown in figure 16.

Arrangements were made, toward the close of the fiscal year, to perform a large part of the remaining small-scale tests in the winter of 1949-50 during periods of gas withdrawal at high rates from the Goleta, Calif., storage reservoir of the Pacific Lighting Corp. Daily rates of flow up to 150,000,000 cubic feet at pressures up to 1,000 p.s.i. are available, far exceeding those available at the Government's Cliffside field, Texas, where all tests to date have been made. The higher flow rates and pressures are necessary to achieve Reynolds numbers in excess of present commercial practice, particularly in the superfinished experimental line and the 6- and 8-inch commercial-pipe experimental lines.

Removal of Excess Nitrogen from Natural Gas

Since February 1947, the Bureau of Mines, in cooperation with the American Gas Association, has been conducting research to develop a practical means for removing excess nitrogen from natural gas. Objectives of the work are the investigation or development of economical means for removing excess nitrogen - normally defined as 10 percent or more - from certain nitrogen-bearing natural gases. Nitrogen is inert and valueless as fuel. Removal of nitrogen from gases at their source in the field would permit substantial increases in the effective deliverability of long transmission lines and permit greater recovery of liquefied petroleum gas (LPG) products without objectionable reduction in the heating value of the gases. Also, it would enhance the marketability of certain gases with such high-nitrogen contents and low-heating values that they find little or no market at present. The work is particularly important with regard to possible removal of nitrogen from gas in the large reserves of the Texas Panhandle and Hugoton fields of Texas, Oklahoma, and Kansas, which contain 12 to 15 percent nitrogen on the average and up to 30 percent in certain areas. It is estimated that many millions of dollars in investment and operating costs could be saved by gas-transmission companies in those fields if an economical method of nitrogen removal were available and applied. The problem is of particular interest to the Bureau in its helium-production activities, because nitrogen is commonly present in quantity in helium-bearing natural gases, and economical disposal of gas after helium extraction may present problems similar to those described.

A preliminary study of the subject, including a survey of literature and patents, indicated that liquefaction and fractionation might be the most favorable method of nitrogen removal. This method is being investigated in a pilot unit at the Bureau's Exell Helium Plant near Amarillo, Tex. The Bureau is unusually well-equipped for the investigation from the standpoints of experienced personnel and availability of low-temperature processing equipment.

The pilot-plant operations are designed to obtain practical information on nitrogen removal, data on a basic nitrogen-removal cycle, and some fundamental engineering data on phase equilibria, heat exchange, thermodynamic properties, and fractionation. Preliminary results have been favorable. Work is being continued to perfect pilot plant operations and extend the data.

HELIUM UTILIZATION AND RESEARCH

Gas Analysis and Helium Survey

The Bureau of Mines carries on a continuous search for natural-gas fields containing commercial quantities of helium. It has been found that almost all natural gases in the United States contain some helium, but the quantity usually is very small, amounting to only a few hundredths or even a few thousandths of a percent. Because only a limited number of natural-gas fields have been found where the helium content of the gas is of the order of 1 percent or more, the Bureau is continually on the alert to discover additional fields containing these relatively high concentrations. Its engineers review reports continuously for information about wildcat wells, new field discoveries, and extensions of old fields. Wherever possible, samples of gas are obtained from these new developments and analyses made for helium content.

Uses of Helium

Helium as a Tracer Gas in Oil and Gas Reservoirs

The Bureau continued its investigation of the use of helium as a tracer gas in oil- and gas-field operations. In this work, helium is mixed in small concentrations with gas that is being injected into reservoirs to increase the recovery of oil or other valuable hydrocarbons. The detection of this tracer helium at various withdrawal wells in the field (fig. 17) reveals valuable information on the direction and rate of movement of gas through the reservoir and reveals information about the reservoir itself that is of great value to the operators of the fields in their unending effort to conserve reservoir energies and increase the ultimate recovery of oil. The Bureau conducted the first few helium-tracer gas projects. Now it provides only a consulting engineering service, available to companies conducting their own helium-tracer gas projects. One project of this type was completed during the year, and consideration is being given to three new projects. Bureau engineers are preparing manuscripts reporting the results of two helium-tracer gas projects.

Helium in Shielded-Arc Welding and Metallurgical Processes

A large percentage of helium now produced is being supplied to industry for welding. Helium shielded-arc welding of aluminum, magnesium, stainless steels, and copper, is now an accepted procedure in industry. This new

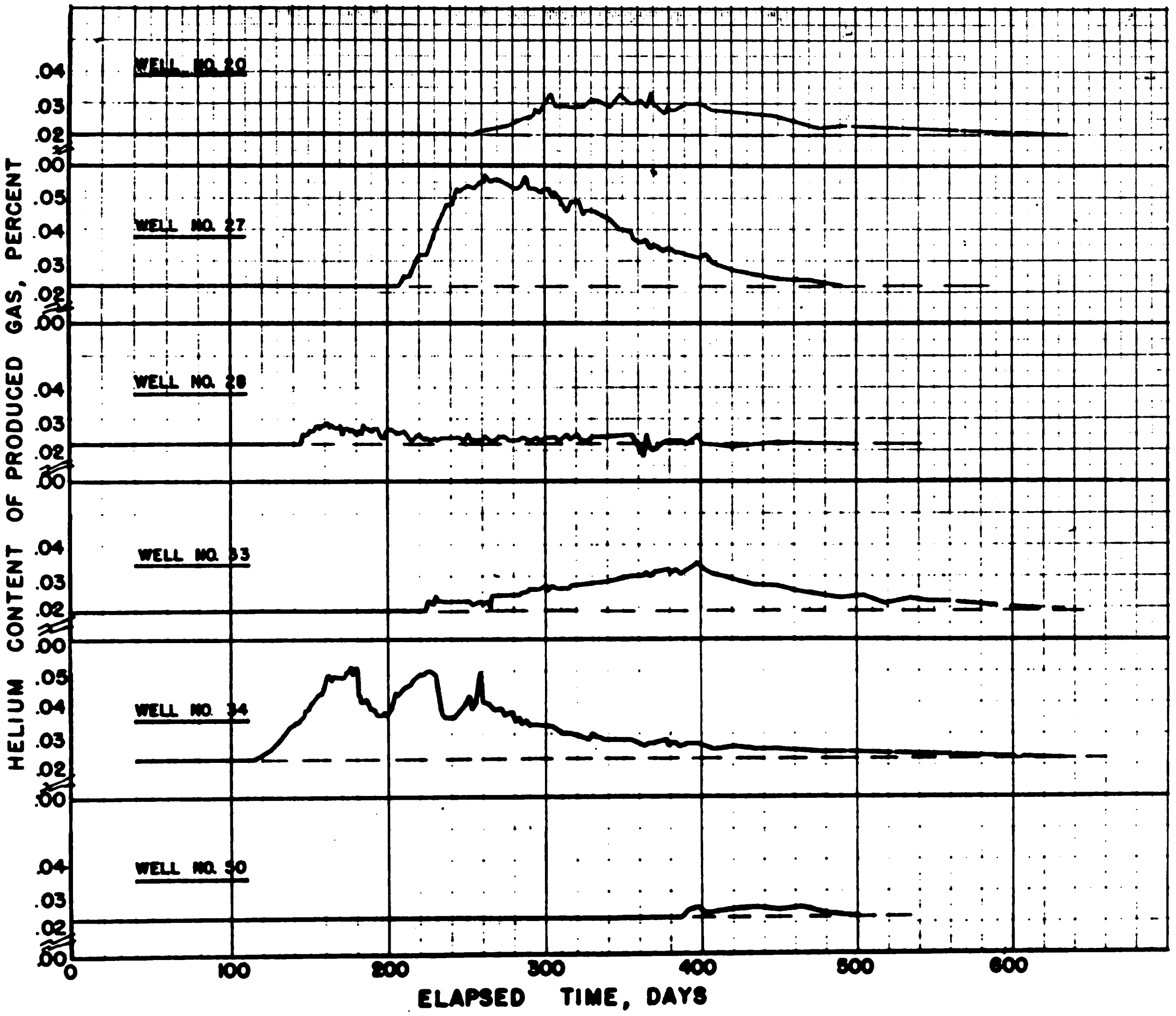

Figure 17. - Graphs illustrating elapsed time and extent of occurrence of helium in gas from producing wells in a helium tracer project.

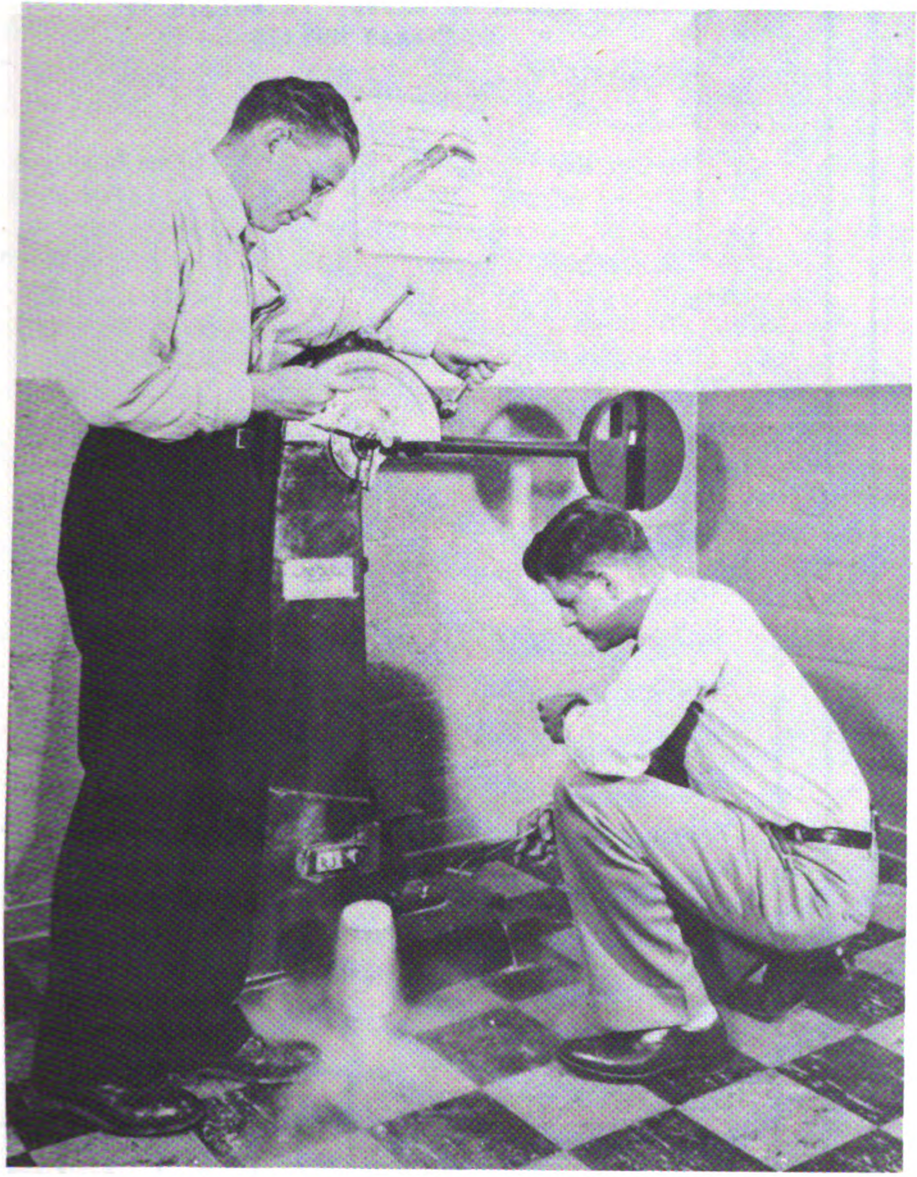

Figure 18. - Low-temperature impact tests on welded stainless steels.

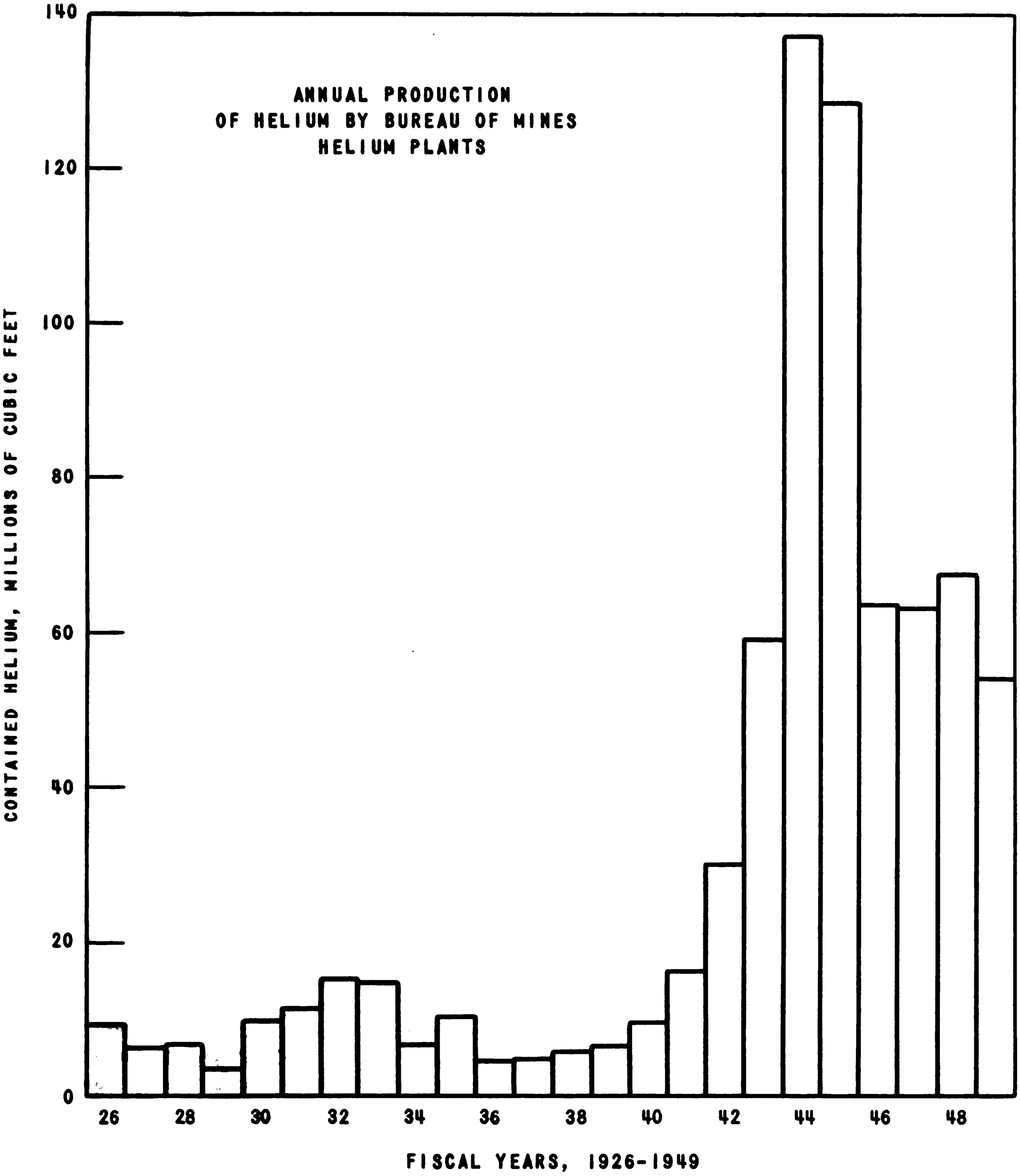

Figure 19. - Yearly volumes of helium produced by the Bureau of Mines.

application for helium is rapidly growing, because it has been found that welding in an atmosphere of helium protects the metals from oxidation and makes denser, stronger welds. The process also has the advantage over other forms of welding, in that no flux or coated electrodes are used.

Investigation has disclosed that welding requires the highest-purity helium available. One phase of the metallurgical program is to set a routine procedure for making weld tests on all helium before it leaves the plant. The weld tests are made by welding aluminum samples on semi-automatic equipment.

Shielded-arc welding requires specialized equipment. Several manufacturers have developed machines for this specific welding process. A number of these machines and electrode holders have been obtained to determine their suitability for inert-arc welding, and welding studies have been made with various combinations of this equipment. Data and information obtained from the welding studies have been furnished to users of helium and others. Several cooperative programs have been arranged with companies and Government agencies that do shielded-arc welding.

The techniques and procedures developed in the helium shielded-arc studies have been used to advantage in the helium plants for welding certain stainless steels and aluminum. These are some of the few metals suitable for extremely low temperatures encountered in helium-extraction operations and similar low-temperature processes.

Metallurgical investigations have been made on materials used in the helium plant. The conditions prevailing in plant operation require metals having good low-temperature properties. Low-temperature studies (fig. 18) are being made on several materials to determine their desirability for use in plant equipment.

HELIUM PRODUCTION AND PROCESS DEVELOPMENT

The Bureau of Mines helium plants are comprised of the Amarillo (Tex.) plant; Exell (Tex.) plant; Otis (Kans.) plant; and Shiprock (N. Mex.) plant. The Amarillo plant is headquarters for direction of all plants and for research activities on helium production, utilization, and related subjects.

During the fiscal year 1949, the Exell plant, the largest of the group, produced all helium required. This plant processes gas enroute to market, so that if the helium were not extracted it would be lost for all time. The plant produced 54,062,443 cubic feet of helium (fig. 19) from 6,501,727,000 cubic feet of natural gas containing about 1 percent helium. The plant shipped 106 tank cars of helium to Federal agencies and 24 tank cars to non-Federal or commercial customers. Since 1926, Bureau of Mines plants have produced over 740,000,000 cubic feet of helium.

All helium was shipped in small cylinders from the Amarillo plant. Helium was transported from the Exell to the Amarillo plant through a Government-owned pipe line. During fiscal year 1949, 40,177 cylinders were shipped to Federal users and 27,108 cylinders to non-Federal users. The plant handled an equal number of cylinders in return shipments and in addition performed extensive work of painting, hydrostatic testing, and other servicing of cylinders. Figure 20 shows the interior of the cylinder-shipping and receiving building at the Amarillo plant. Approximately 2.46 percent more helium was shipped in fiscal year 1949 than in the preceding year. There was a small but notable increase in the amount of helium shipped in tank cars as compared to small cylinders. In spite of continued high-production costs and some additional expenses of processing, as referred to later herein, helium was sold at substantially the same cost to users as in recent years.

The helium pipe line connecting the Exell and Amarillo plants traverses the Government-owned Cliffside field, and means are available for injection and conservation of helium in the field if and when available in excess of demand. During fiscal year 1949, 5,716,700 cubic feet of helium was injected into the field for conservation purposes.

The major development of the year was successful efforts to increase further the purity of produced helium. The purity was raised in the preceding year from 98.2 to about 99.8 percent, and this year to virtually 100 percent. The effort to produce still purer helium was prompted primarily by the results of investigative work in the research laboratory, which showed that very pure helium is highly desirable, if not absolutely necessary, for use in shielded-arc welding, the fastest growing use for helium. Most of the investigative work to increase the purity was done at the Amarillo plant in order to avoid any interruption to production activities at the Exell plant. The means developed for the purpose involve additional provisions for passage of helium over charcoal refrigerated to the temperature of liquid nitrogen. The demand from the welding industry and some other Federal and non-Federal users for helium of the higher purity was so immediate that the development unit was pressed into actual production operations, and approximately 13,200,000 cubic feet of this high-purity helium was shipped from the Amarillo plant during the last 6 months of the fiscal year. At the close of the year, a similar full-scale production unit was installed at the Exell plant to permit production there of this high-purity product. The high-purity helium is identified as "double-charcoal purified helium," inasmuch as the production process involves passage of the helium through refrigerated charcoal at two selected temperature levels.

A problem related to production and shipment of high-purity helium is that of cleaning shipping containers to remove any oil, water, and other contaminating substances. This is necessary to make sure that users receive the high-purity helium without contamination in shipment. In this program, a number of Navy tank cars and small cylinders were internally washed with a hot solution of soap and water, rinsed with clean water, and dried. All shipping containers are now evacuated, purged, re-evacuated and purged again before final charging with pure helium. Production of the higher-purity helium and the preparation of clean shipping containers have caused a substantial increase in the work load and the cost of helium production, but this has been absorbed to make the higher-purity helium available without an increase in price over the previous product.

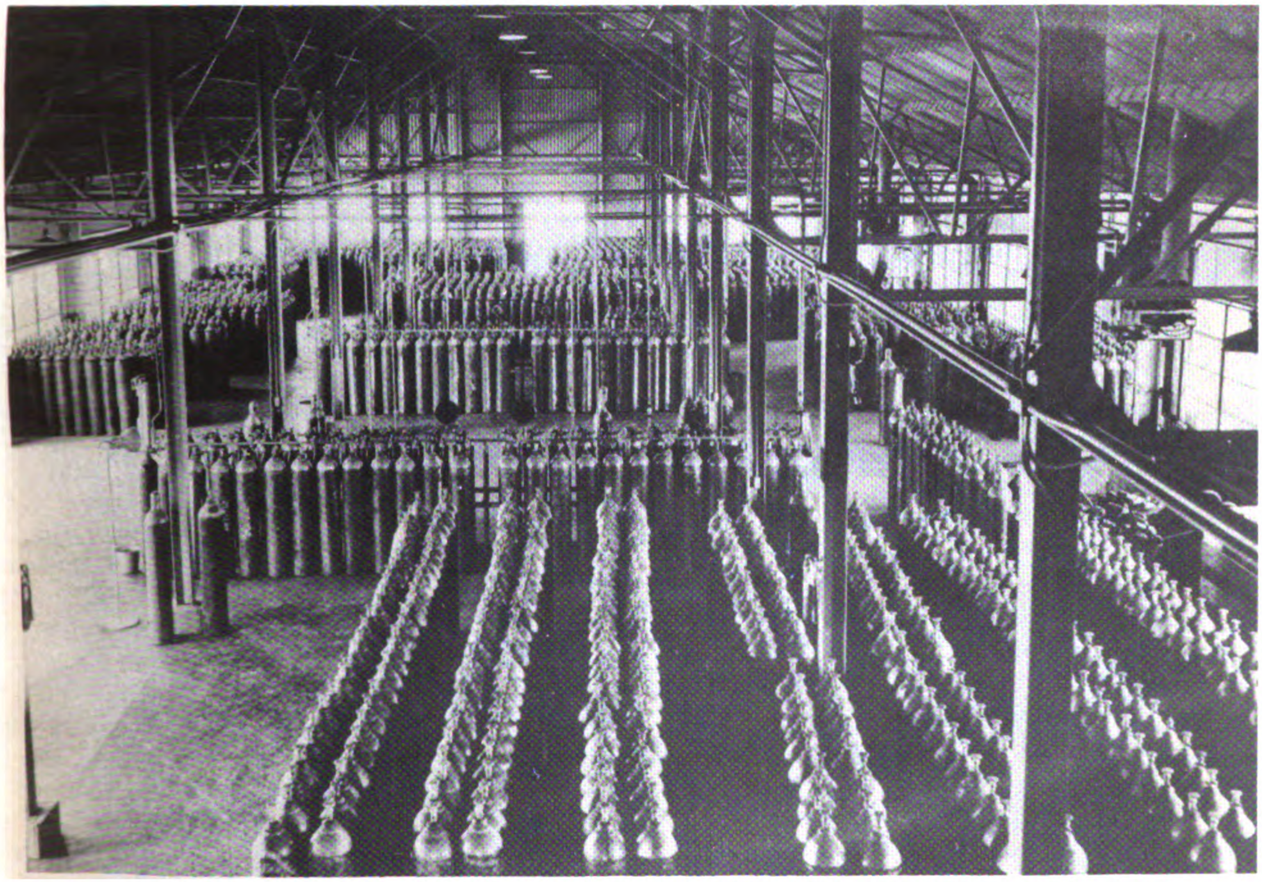

Figure 20. - Interior view of cylinder shipping and receiving building at Amarillo Helium Plant.